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LIST OF ABBREVIATIONS

EGDM : Ethylene glycol dimethacrylate
AIBN : 2,2'-azobisisobutyronitrile

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LIST OF SYMBOLS

v_2	Volume fraction of crosslinked polymer in the gel, i.e., inverse of the volume swelling ratio q_v
χ	Polymer-solvent interaction parameter
$\overline{M_c}$	Molecular weight of the polymer chains between two successive effective crosslinks, i.e., the molecular weight of the network chains
v_2^0	Volume fraction of the crosslinked polymer after the gel preparation
f	Mole fraction of ionic segments in the network chains
ρ	Density of dry network
G	Elastic modulus of gel after their preparation
f	Stress
α	Deformation ratio (deformed length /initial length)
A	Front factor
R_θ	Rayleigh ratio
I_θ	Intensity of scattered light at the angle θ
I_0	Intensity of incident light beam
θ	Observation angle (Scattering angle)
V	Volume of scattering medium
r	Distance between the scattering volume and detector
q	Scattering vector amplitude
n	Refractive index of the medium
λ	Wavelength of radiation
ξ	Correlation length
R_{ex}	Excess scattering
K_{DB}	Optical constant
n_o and n_i	Refractive indices of solvent and polymer
$\gamma(r)$	correlation function
η_1 and η_2	Fluctuations in the refractive index measured in point 1 and point 2.
$\langle \eta^2 \rangle$	The mean square refractive index fluctuations
$(v_2)_A$ and $(v_2)_B$	Polymer concentrations in A and B regions.
Δv_2	Difference of polymer concentration between the regions A and B.
V_l	Molar volume of solvent
v_2^0	Volume fraction of the crosslinked polymer after the gel preparation

qF	Mass swelling ratio after the gel preparation (mass of gel after preparation /mass of dry gel)
d_1	Density of solvent
V_o, V	Gel volumes after the gel preparation and after swelling
D, D_o	Diameter of the gels after equilibrium swelling and after preparation
q_v	Volume swelling ratio
F	Force
A	Cross-sectional area
g	Gravitational acceleration
l_o, l	Initial undeformed and deformed lengths
$\overline{M}_{c,chem}$	Chemical value of \overline{M}_C
$\overline{M}_{c,eff}$	Effective value of \overline{M}_C
C_0	Initial monomer concentration of monomers
V_r	Molar volume of polymer repeat units
X	Crosslinker ratio
M_r	Molecular weight of polymer repeated units.

SUMMARY

DETERMINATION OF SPATIAL INHOMOGENEITY IN POLYSTYRENE GELS BY USING STATIC LIGHT SCATTERING TECHNIQUE

The aim of this study is to determine the degree of spatial inhomogeneity in polystyrene gels by static light scattering technique at a gel state just after their preparation.

In this study, the gels were prepared by free radical crosslinking copolymerization of styrene and ethylene glycol dimethacrylate (EGDM) crosslinker. The extent of spatial inhomogeneity in polystyrene gels was investigated as a function of the gel synthesis parameters. The experimental parameters varied were: the crosslink density, the kinetic chain length and the solvent quality. A variety of synthesis conditions has been applied to obtain polymer gels with different degree of inhomogeneity. The excess scattering of polystyrene gels was determined by subtracting the scattering intensity of an uncrosslinked polystyrene solution with the same polymer concentration from the scattering intensity of the gel. The excess scattering of polystyrene gels is taken as a measure of their inhomogeneity. The light scattering data were also analyzed within the framework of the Debye-Bueche theory. The gels were characterized by the swelling and elasticity tests as well as the static light scattering measurements at a gel state just after their preparation.

The results of the static light scattering experiments showed that the degree of spatial gel inhomogeneity increases with increasing crosslinker (EGDM) concentration and with decreasing quality of polymerization solvent. The degree of spatial gel inhomogeneity decreases with drying of the gels and with increasing amount of the chain transfer agent present in the gel formation process. It was also observed that there is a direct correlation between the scattering features of gels and their elastic properties. During the free-radical crosslinking copolymerization of styrene and EGDM, the distance between the pendant vinyl groups locating on the same molecule varies depending on the synthesis parameters. As the distance between pendant vinyl groups in the gel formation system increases, the number of multiple crosslinking necessarily decreases so that the gels formed become increasingly homogenous. Finally, the experimental findings suggest that the factors increasing the distance between the pendant vinyl groups decrease the number of multiple crosslinks so that the degree of the spatial gel inhomogeneity also decreases. In order to obtain gels with a minimum degree of spatial gel inhomogeneity, one should reduce the effective crosslink density of gels by (a) decreasing the crosslinker concentration, (b) adding a chain transfer agent in the gel formation system, or (c) using a good solvent as the medium of the crosslinking copolymerization.

ÖZET

POLİSTİREN JELLERİNDEKİ YAPISAL İNHOMOJENİTENİN STATİK IŞIK SAÇINIMI TEKNİĞİ İLE SAPTANMASI

Bu çalışmanın amacı polistiren jellerinin sentez sonrası durumlarındaki inhomojenite derecelerinin statik ışık saçınımı tekniği ile incelenmesidir.

Polistiren jelleri stiren monomeri ile etilen glikol dimetakrilat (EGDM) çapraz bağlayıcısının serbest radikal mekanizma ile kopolimerizasyonu sonucu elde edilmiştir. Senez şartlarına bağlı olarak polistiren jellerindeki inhomojenite dereceleri incelenmiştir. Bu amaçla, çapraz bağlayıcı konsantrasyonu, kinetik zincir uzunluğu ve çözücü kalitesi gibi sentez parametreleri değiştirilerek farklı inhomojenite derecelerine sahip jeller elde edilmiştir. Polistiren jellerindeki fazla saçınım, jel örneklerinden saçınma intensitileri ile aynı monomer konsantrasyonunda sentezlenen polistiren çözeltilerinden saçınan ışık intensitileri arasındaki farktan hesaplanmıştır. Jellerdeki fazla saçınım değerleri ile jellerin inhomojenite dereceleri saptanmıştır. Ayrıca polistiren jellerinden ölçülen fazla saçınım değerlerinden Debye-Bueche denklemi yardımı ile jeller için önemli olan parametreler hesaplanmıştır. Statik ışık saçınımı ölçümlerinin yanında, jeller şişme ve elastik modül ölçümlerine de tabii tutulmuştur.

Yapılan çalışmalar sonucunda polistiren jellerinin inhomojenite derecelerinin çapraz bağlayıcı (EGDM) konsantrasyonunun arttırılması ve çözücü kalitesinin azaltılması ile arttığı gözlenmiştir. Aynı zamanda polimerizasyon sırasında zincir transfercisinin kullanılması ve jellerin büzülmesi durumlarında ise jellerin inhomojenite derecelerinin azaldığı saptanmıştır. Jellerin ışık saçınım ve elastise özellikler arasında benzerlik olduğu da bulunmuştur. Son olarak, çok katlı çapraz bağlanma reaksiyonlarının artmasının jel inhomojenitesini arttırdığı saptanmıştır. Stiren ile EGDM in serbest radikal mekanizma ile kopolimerizasyonu sırasında büyüyen zincir üzerindeki asılı vinil gruplar arasındaki mesafenin sentez şartlarına bağlı olarak değiştiği saptanmıştır. Asılı vinil grupları arasındaki mesafenin arttırılmasının çok katlı çapraz bağlanma reaksiyonlarının azalmasını dolayısı ile jel inhomojenitesinin azalmasına neden olduğu saptanmıştır. Jellerdeki inhomojenite derecelerinin jellerdeki efektif çapraz yoğunluğunun azalması: (a) çapraz bağlayıcı konsantrasyonunun azaltılması, (b) polimerizasyon sırasında zincir transfercisinin kullanılması ve (c) polimerizasyon çözücüsünün kalitesinin arttırılması ile sağlanacağı gösterilmiştir.

1. INTRODUCTION

A polymer gel is a network of flexible chains showing both liquid-like and solid-like properties. The liquid like properties result from the fact that the major constituent of gel is a liquid. For example, jelly consists of approximately 97 % of water and 3 % gelatin. The properties of a gel depend strongly on the interactions of its two components, namely, the solvent and the polymer network. The liquid prevents the polymer network from collapsing into a compact mass, whereas the network prevents the liquid from flowing away. On the other hand, a gel can retain its shape since it has a shear modulus which becomes apparent when the gel is deformed. The modulus is due to the crosslinking of the polymer into an infinite network. These aspects of a gel represent the solid nature of gels [1,2].

Polymeric gels have a wide range of applications as ion-exchange resins, absorbents, superabsorbents, biomimetic materials, chemomechanical actuator, optical devices, new type of food and soil modifiers, etc. For example, gels are used as a molecular sieve for molecular separation, such as in gel permeation chromatography and electrophoresis [3].

Gels may be indistinguishable with the corresponding polymer solutions on the scale at several nanometers. However, if we zoom out the view to a distance comparable to the inter-crosslink distance, we should observe that the effects of crosslinks play an important role in the physical properties of gels. It is easy to envisage that polymer chains are instantaneously frozen at the gel point, leading to an emergence of non-cancelled-out concentration fluctuations, i.e. an appearance of inhomogeneous structure [4].

Polymer gels can be prepared by chemical or physical crosslinking processes. Most of the gels are prepared by a chemical crosslinking process induced by free radicals, called free radical crosslinking polymerization. Here, a monovinyl monomer and a divinyl monomer (crosslinker) is copolymerized in the presence of a free radical initiator. In contrast to perfect networks with a constant chain length between

crosslinks, real networks formed by free-radical mechanism exhibit a wide chain length distribution between the junction points. Furthermore, in a perfect network, it is assumed that all the crosslinker molecules are consumed by effective crosslinking reactions and act as effective junction points (Fig.1.1A).

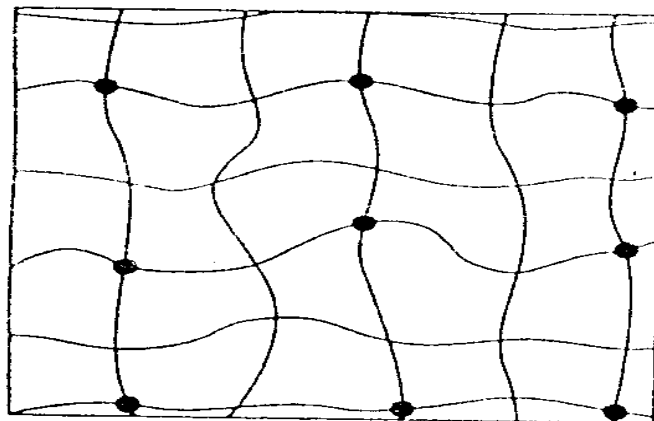


Fig 1.1.A: Schematic representation of an ideal gel.

However, a variety of network defects and nonidealities such as dangling chains, elastically ineffective loops (cycles), the different and conversion-dependent vinyl group reactivities, cyclization, multiple crosslinking and diffusion-controlled reactions are known to occur [5-7]. These defects change the effective crosslinking density of gels and thus influence their elastic properties as well as swelling behavior. As a result, theories are still unable to predict the physical properties of gels from their synthesis parameters.

One of the network defects, which has been extensively studied, is the gel inhomogeneity [3,8]. The spatial inhomogeneity means the fluctuations of crosslink density in polymer gels. These can be visualized as strongly crosslinked regions in a less densely crosslinked environment. The higher the crosslink density, the lower is the swelling capacity. As a result, an inhomogeneously crosslinked gel consist of regions with relatively high polymer concentration and more swollen or diluted regions with lower polymer concentration. Figure (1.1B) shows a schematic picture of an inhomogeneously crosslinked gel. Regions with higher local crosslink density are marked by dashed lines.

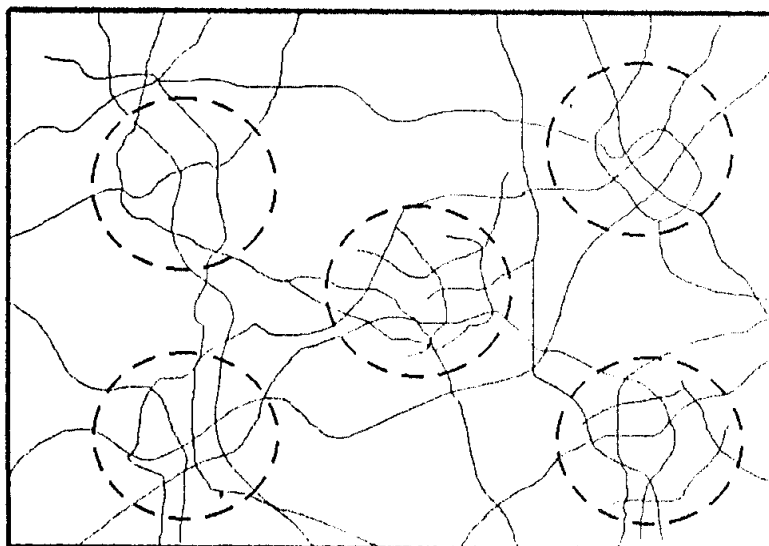


Fig 1.1.B: Schematic representation of an inhomogeneously crosslinked gel [9].

The understanding of the spatial gel inhomogeneity is very important from both scientific and engineering point of view. For example, (i) The mechanical properties of elastomers can be improved by controlling the spatial inhomogeneity, (ii) the control of mesh size of gel matrix is crucial for electrophoresis and (iii) the optical haze of contact lenses can be suppressed by reducing the spatial inhomogeneity [3]. Since the gel inhomogeneity is closely connected to the spatial concentration fluctuations, scattering methods such as light scattering, small-angle X-ray scattering, and small-angle neutron scattering have been employed to investigate the spatial inhomogeneities [10-15]. The gel inhomogeneity can be manifested by comparing the scattering intensities from the gel and from a semi-dilute solution of the same polymer at the same concentration. The scattering intensity from gels is always larger than that from the polymer solution. The excess scattering over the scattering from polymer solution is related to the degree of the inhomogeneities in gels.

The excess scattering intensity from polymer gels, has been found to depend on the gel preparation method [8], the crosslink density [16-20], the swelling ratio [8,20], and the degree of ionization [3,8,21]. In general, the gel inhomogeneity increases significantly with the crosslink density. A reduced reactivity of the crosslinker used in the gel preparation also leads to a higher degree of inhomogeneity [5]. On the other hand, the inhomogeneity decreases with the ionization degree of gels. An

enhancement of the excess scattering is generally observed, if the gel swells beyond its swelling degree after preparation.

The aim of this study is to determine the degree of spatial inhomogeneity in polystyrene gels by static light scattering technique at a gel state just after their preparation. The gels were prepared by free radical crosslinking copolymerization of styrene and ethylene glycol dimethacrylate (EGDM) crosslinker. The spatial inhomogeneity in polystyrene gels was investigated as a function of a number of parameters, i.e., the initial monomer concentration, the crosslink density, the kinetic chain length and the solvent quality. A variety of synthesis conditions has been applied to obtain polymer gels with different degree of inhomogeneity. The excess scattering of polystyrene gels was determined by subtracting the scattering intensity of an uncrosslinked polystyrene solution with the same polymer concentration from the scattering intensity of the gel. The excess scattering of polystyrene gels is taken as a measure of their inhomogeneity. The gels were also characterized by the elasticity test. As will be shown below, several interesting phenomena were observed such as the decrease of the degree of the spatial gel inhomogeneity with decreasing primary chain length of polymer network and with increasing solvating power of the polymerization solvent. The results were explained in terms of the inhomogeneity parameters of the Debye-Bueche theory, i.e., the mean square fluctuations of the refractive index $\langle \eta^2 \rangle$ and the correlation length of the scatterers ξ .

2. GELS

The mechanical properties of polymer networks are well understood. In case of a small deformation, the elastic behavior of gels can be described using the theory of statistical rubber elasticity. By measuring the modulus of gels, one can get the number of elastically effective network chains, ν_e , or, the molecular weight between two successive crosslink points, \overline{M}_c , which are characteristic sizes of polymer networks [22].

Although the macroscopic properties of gels are examined in detail since the early 40 ties, little information is available about microscopic changes in particular the structural changes during the deformation process [23]. The microscopic properties of gels include complexity in chemistry, statistical mechanics and nonequilibrium nature of the crosslinking process and/or in the resultant polymer networks [3]. From the scattering experiments, it is possible to distinguish the microstructures of gels.

As reported before, polymer gels have two types of concentration fluctuations; liquidlike and solidlike fluctuations. The former are time-dependent (thermal) fluctuations which are comparable to those of polymer solutions and the latter are time-independent spatial inhomogeneities [3,17]. The appearance of crosslink (spatial) inhomogeneity is a result of topological freezing of chains by crosslinking [3,8,17]. It is assumed that the network is formed instantaneously, or in a short period of time. The dynamics of the concentration fluctuations of the pre-gel solution of monomers can be considered as topologically ‘frozen’ in the final network structure. In addition, owing to the crosslinking process the polymer chain distribution in the network tends to increase the local polymer concentration in the vicinity of junctions, compared with the mean polymer concentration in the gel [24].

The spatial gel inhomogeneity is as a result of the random, non-homogeneous character of the crosslink placement within the polymer. That is to say, since the crosslink points are placed into the polymer in a random configuration, certain regions (clusters) of network will have higher crosslink density than do others [25]. Such interconnected clusters are looked like ‘islands’ in a three-dimensional solvent

‘sea’ [26-30]. They cannot change its concentration easily upon a change of the overall concentration by swelling or deswelling. In the swelling state of a gel, these crosslinks cannot move apart from the each other since they are connected by a chain segment which is in optimal excluded volume conformation. Most of swelling will presumably be accounted for by the less crosslinked regions between the clusters. As a result, one may expect that the swelling of a network is very inhomogeneous due to the appearance of clusters forming regions ‘harder’ than average. Swelling must therefore lead to an enhancement of the polymer concentration difference between the cluster and the interstitial regions. Thus, strong scattering appears by swelling [8,20,31]. This mechanism is represented schematically in Fig 2.1.

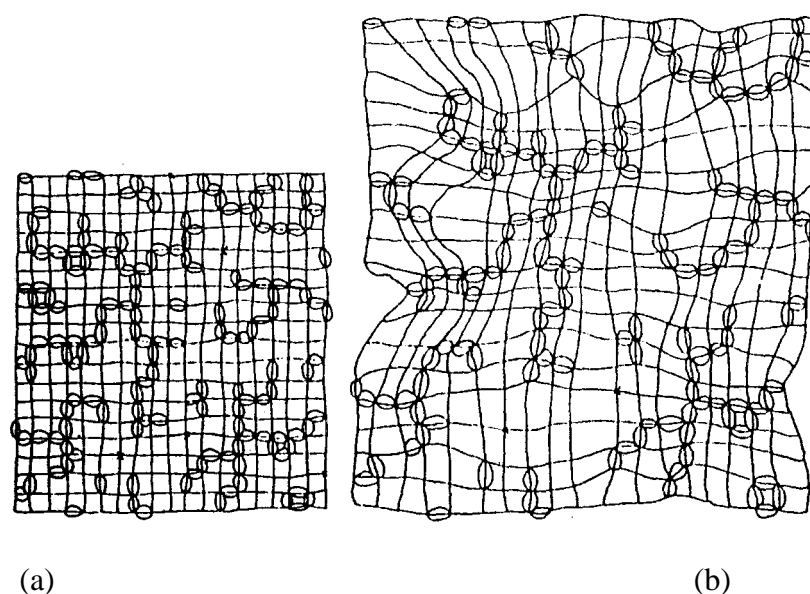


Figure 2.1: Schematic representation of a gel prepared by random crosslinking of a semi-dilute solution. Clusters are represented by sign: \ominus (a) In the preparation state; (b) after inhomogeneous swelling with respect to the preparation state [8].

Inhomogeneities appearing in gels prepared by random crosslinking of a semi-dilute polymer solution depend strongly on the condition at the gel preparation and on the chemistry of crosslinker. According to Baselga et al., the difference between the reactivities of monomeric vinyls is the reason for the inhomogeneous network structure [32]. Recent studies, however, indicate the existence of intramolecular crosslinking reactions in the form of cyclization and multiple crosslinking, which are responsible for these inhomogeneities [33,34]. Moreover, a strong steric excluded-

volume effect preventing the pendant vinyl groups from reacting seems to be the another reason for the inhomogeneous network structure [33].

The inhomogeneities present in gels are of considerable importance in study of the physical properties such as swelling, optical and mechanical properties of these materials. Using the modern theories of gels and new methodologies such as small-angle neutron scattering and light scattering, the microscopic structure of gels becomes clearer and the nature of gels is better understood. The microscopic gel science introduced here is strongly linked to other fields of science and/or engineering, such as biology, medical science, food science, mechanical engineering, civil engineering etc. [3].

2.1 Swelling of Gels

Polymeric gels absorb large quantities of suitable solvents without dissolving. As more and more solvent is absorbed by the polymer network, the network expands progressively. During the swelling process, the network chains are forced to attain more elongated, less probable configurations. As a result, like pulling a spring from both ends, a decrease in chain configurational entropy is produced by swelling. Opposing this, an increase in entropy of mixing of solvent with polymer accompanies the swelling. In addition, enthalpy of mixing also controls the extent of swelling.

The equilibrium swelling theory developed by Flory and Rehner treats simple polymer networks in the presence of small molecules. The theory considers forces arising from three sources:

- (1) The entropy change caused by mixing polymer and solvent. The entropy change from this source is positive and favors swelling.
- (2) The entropy change by reduction in the number of possible chain conformations on swelling. The entropy change from this source is negative and opposes swelling.
- (3) The heat of mixing of polymer and solvent, which may be positive, negative, or zero. Usually, it is slightly positive, opposing mixing.

The Flory - Rehner equation including the Donnan equilibria for ionic gels may be written for an affine network as follows [35]:

$$\ln(1-\nu_2) + \nu_2 + \chi \nu_2^2 + \frac{\rho}{\overline{M}_c} V_1 \left(\nu_2^{1/3} \nu_2^{0/3} - \nu_2/2 \right) - f \nu_2 = 0 \quad (2.1)$$

where ν_2 is the volume fraction of polymer in the swollen gel, i.e., inverse of the volume swelling ratio q_v ,

χ is the polymer - solvent interaction parameter,

\overline{M}_c is the molecular weight of polymer chains between two successive effective crosslinks, i.e., the molecular weight of the network chains

ν_2^0 is the volume fraction of crosslinked polymer after the gel preparation,

f is the fraction of ionic units in the polymer, and

ρ is the density of dry network.

2.2 Elastic Deformation of Gels

The mechanical properties of polymer networks can be determined by stress-strain measurements. Figure 2.2 shows a typical stress-strain apparatus. The apparatus is used to measure the force required to give a specified elongation in a sample. The force acting on sample is generally in unit newton (N) and the nominal or engineering stress f (the force divided by the undeformed cross-sectional area) is in N/m^2 (Pa) [36].

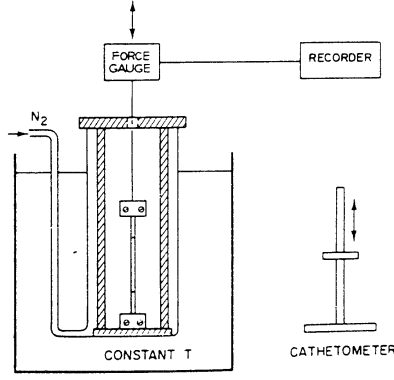


Figure 2.2: Apparatus for carrying out stress-strain measurements [36].

For a homogenous network of Gaussian-chains, stress-strain relation for uniaxial deformation is given by [35]:

$$f = G(\alpha - \alpha^{-2}) \quad (2.2)$$

where α is the deformation ratio (deformed length/initial length) .

In equation (2.2) G represents the elastic modulus of gels. The elastic modulus G can be determined from the slope of the linear f vs. $\alpha - \alpha^{-2}$ dependence. Elastic modulus of swollen gels G relates to the network crosslink density through the equation [22, 35]:

$$G = A \frac{\rho}{M_c} RT \nu_2^{1/3} \nu_2^{0/3} \quad (2.3)$$

where, the front factor A equals to 1 for an affine network and $1-2/\phi$ for a phantom network, ϕ is the functionality of the crosslinker.

As shown in equation (2.3), the elastic modulus, G , increases as the effective crosslink density of the network is increased or, as the swelling ratio of gel subjected to the elasticity test is decreased.

3. LIGHT SCATTERING

3.1 Light Scattering:

Scattering of light by any system is related to the heterogeneity of that system. Heterogeneity may appear on the molecular scale or on the scale of aggregations of many molecules. Regardless of the type of heterogeneity, the underlying physics of scattering is the same for all systems. Matter is composed of discrete electric charges: electrons and protons. If an obstacle, which could be a single electron, an atom or molecule, a solid or liquid particle, is illuminated by an electromagnetic wave, electric charges in the obstacle are set into oscillatory motion by the electric field of the incident wave. Accelerated electric charges radiate the electromagnetic energy in all directions; it is the secondary radiation that is called the radiation scattered by the obstacle.

In the analysis of the interaction of a beam of light with an optically smooth interface, it is assumed that the refracting medium is perfectly homogenous. In fact, it is only statistically homogeneous, that is, the average number of molecules in a given volume element is constant, but, at any instant, the number of molecules in this element will be different compared with any other instant. It is the density fluctuations which give rise to scattering in optically dense media such as solids, liquids and many gasses in which the molecular separation is much less than the wavelength of the incident light. There are also other types of fluctuations. For example, if sugar is dissolved in water, after thorough stirring, the sugar concentration will be statistically homogeneous, but concentration fluctuations will give rise to scattering. If the molecules are nonspherical, there will be orientation fluctuations [37].

The first quantitative study on the scattering by small particles was made in 1871 by Rayleigh. The mathematical investigation of the problem gave a general law for the intensity of scattered light, applicable to any particle having refractive index which is different from that of the surrounding medium. The only restriction is that the linear

dimensions of the particles be considerably smaller than the wavelength of light. The scattering light intensity is found to be proportional to the incident light intensity and to the square of the volume of the scattering particle. The most interesting result is the dependence of the scattered light intensity on the inverse of the fourth power of wavelength λ^{-4} [38].

It is well known that light scattering causes opalescence when a light beam passes through a solution. Light scattering is caused by density and concentration fluctuations; i.e., by the deviation of density and concentration from their uniform values in a dispersed medium. Light is scattering only when a light wavelength, λ , is greater than the size of a particle of the dispersed phase. If λ is much greater than the particle diameter, the scatterer can be viewed as a point of source and the corresponding scattered radiation is known as Rayleigh scattering. There will be no angular variation in the amount of scattered light (Fig.3.1). When the size of particles in the dispersed medium becomes much greater than λ , light is not more scattered but reflected [39].

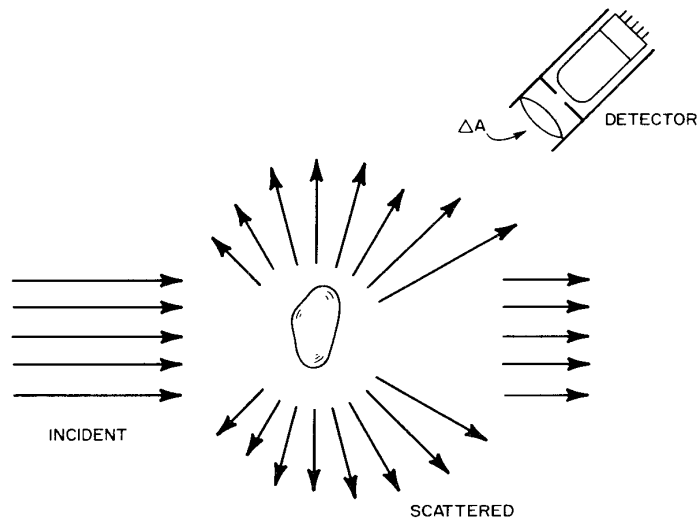


Figure 3.1: Scattering of light by a particle of a size smaller than wavelength [37].

When a beam of light passes through matter, most of the light continues in its original direction. However, some of the light is scattered into new directions. The amount and angular distribution of the scattered light by the particle depends in a

detailed way on the nature of the particle, that is, its shape, size and, the materials of which it is composed [37].

Since its early development by Einstein, Raman, Debye, Zimm and others, the theory of light scattering from macromolecular solutions and suspensions has represented one of the major successes of chemical physics. Indeed, light scattering is one of the few absolute methods available for the determination of molecular mass and structure [40].

The actual measurement of scattered light depends on several factors, including the angle, distance from detector to scattering volume, incident light intensity and the volume of sample illuminated [38]. The symbol used to describe the angle-dependent light scattering is R_θ , called the Rayleigh ratio. It is defined as:

$$R_\theta = \frac{I_\theta}{I_0 V} r^2 \quad (3.1)$$

where I_θ is the intensity of scattered light at the angle θ , I_0 is the intensity of the incident light beam, V is the volume of the scattering medium and r is the distance between the scattering volume and the detector (Fig. 3.2).

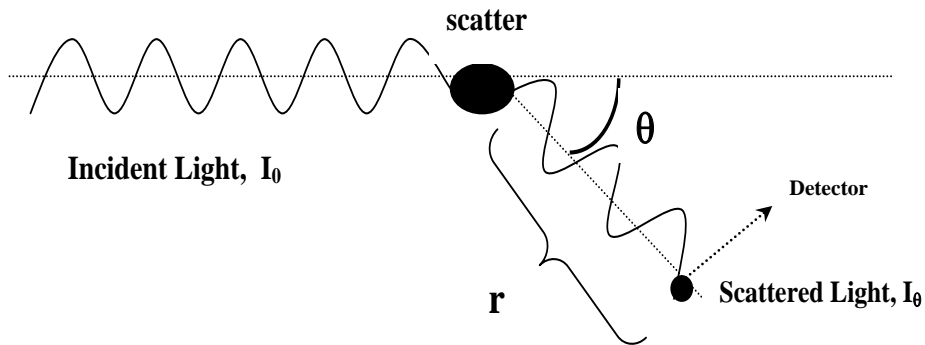


Figure 3.2: Schematic representation of a light scattering model.

3.2 Scattering from Polymer Solutions

When a monochromatic, coherent beam of light is incident a dilute solution of macromolecules, and if the solvent refractive index is different from that of the solute (macromolecules), the incident light is scattered by each illuminated macromolecule in all directions. The scattering light waves from different macromolecules mutually interfere, or combine, and finally produce a net scattering intensity $I(t)$ at a given instant, that are not uniform on the scattering (or direction) plane. If all the macromolecules are stationary, the scattering light intensity at each direction would be a constant i.e., independent of time. However, in reality, all the scatterers in solution are undergoing constant Brownian motions, and this fact leads to fluctuations of the scattered intensity pattern on the detection plane and the fluctuation in $I(t)$ if the detection area is sufficiently small. The fluctuation rates can be related to different relaxation processes such as translational and rotational diffusions as well as internal motions of macromolecules. The faster relaxation process, the faster intensity will be [41].

In polymer science, light scattering is normally referred to in terms of static (elastic) or dynamic (quasi- elastic) measurements, or both [42]. Static light scattering as a classic and absolute analytical method measures the time- average scattered intensity, and it has been widely used to characterize synthetic and natural macromolecules [43]. On the other hand, dynamic light scattering measures the intensity fluctuations instead of the average light intensity (this is where the word dynamic comes from), and its essence may be explained as follows: When the incident light is scattered by a moving macromolecule or particle, the detected frequency of the scattering light will be slightly higher or lower than the original incident light, depending on whether the particle moves toward or away from the detector.

Depending on the concentration, polymer solutions can be separated into three groups: dilute, semi-dilute and concentrated solutions (Fig.3.3) [44].

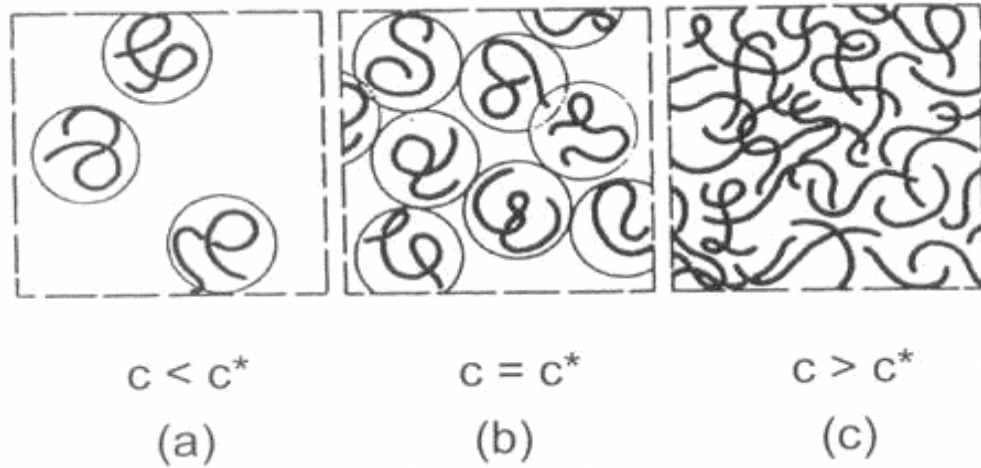


Figure 3.3: Crossover between dilute and semi-dilute solutions: (a) dilute, (b) onset of overlap, and (c) semi-dilute [44].

In dilute polymer solutions, different macromolecules do not overlap and their physical properties can be considered as single chain properties (Fig.3.3 a). As the concentration is increased, the volume fraction occupied by chains in the solution becomes larger and interchange interactions are more and more relevant. As long as the volume fraction occupied by the chains is much smaller than one, solutions may be considered as a gas of chains. When the volume fraction occupied by the chains is of the order of one, the chains overlap and one cannot consider them individually; their behavior becomes cooperative.

A fundamental distinction exists between dilute polymer solutions where the coils are separate (Fig. 3.3a) and more concentrated solutions where the coils overlap (Fig. 3.3c). At the overlap threshold ($c = c^*$) the coils begin to be densely packed [44] (Fig. 3.3c). For solutions of polymer molecules of a high degree of polymerization N , the overlap concentration c^* , expressed as the volume fraction of the monomers, is much smaller than 1. Therefore, there exist a broad range of monomer concentration c where the coils do overlap but where the concentration c is still low:

$$c^* \ll c \ll 1$$

This regime is called semi-dilute regime where the chains overlap and make a dilute physical network in the solvent. The semi-dilute regime is of great interest for two reasons [44].

- a) It corresponds to a large fraction of the c interval in high polymer solutions,
- b) Since $c \ll 1$, the monomer-monomer interactions can be described very simple, much like the interactions in an imperfect, dilute gas.

A semi-dilute polymer solution shares many properties with the polymeric gels. For example, when a semi-dilute solution is photographed at a certain time, this looks like a network with a certain average mesh size ξ (Fig. 3.4). However, the major difference between a semi-dilute solution and gel is that, the chains in solution constantly fluctuate and thus, the entanglements between different chains playing the role of crosslinks have a short life time. For many purposes, an equivalent semi-dilute polymer solution can thus serve as a guide and as a reference in the understanding of the physical properties of polymer gels [8]. Such a system can be characterized by the correlation length ξ beyond which the chains are interpenetrated and the polymer concentration is nearly homogeneous. In a good solvent, the correlation length ξ is roughly equal to the average distance between the interchain contact points [20,44].

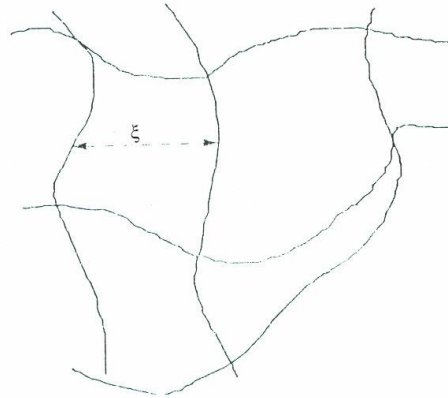


Figure 3.4: A scheme of a semi-dilute polymer solution with correlation length ξ [8,44,45] .

For semi-dilute polymer solutions, the scattering light intensity is given by a Lorentz function [3, 44]:

$$I_{soln}(q) = \frac{I_{soln}(0)}{(1 + q^2 \xi^2)} \quad (3.2)$$

where $I_{soln}(q)$ is the intensity of scattered light at q , $I_{soln}(0)$ is a constant and equals to $I_{soln}(q=0)$, q is the scattering vector amplitude,

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (3.3)$$

λ is the wavelength of the radiation used in the experiment, n is the refractive index of the medium and θ is the scattering angle, that is, the angle between the direction of the incident beam and observation. According to equation (3.2), as the correlation length ξ or the scattering angle θ (or q) is increased, the scattering light intensity $I_{soln}(q)$ decreases .

4. SCATTERING FROM GELS

As reported before, a gel scatters much more light than an uncrosslinked polymer solution at the same concentration [3-5,8-19,46-49]. The increase in the scattering has been attributed to the spatial gel inhomogeneities i.e., to the inhomogeneous distribution of crosslink points in the gel sample [3,8]. The existence of spatial inhomogeneities at submicrometer scales in gels is mainly a result of the gel formation mechanism by free-radical crosslinking copolymerization (FCC). The most important reasons for the formation of an inhomogeneous network structure are:

1-Higher reactivity of crosslinker molecules with respect to the monomer molecules [32]: The reactivity ratios of crosslinker (divinyl) molecules are usually larger than the monomer (vinyl) molecules. Thus, in copolymerization, the growing chains in the pregel stage are rich in crosslinker units because of the higher reactivity of the crosslinker units. As a consequence of this unequal vinyl group reactivity, the crosslink density of gels fluctuates. Computer simulation results also show that there is indeed an influence of the crosslinker reactivity on the extent of the concentration fluctuations in gels [50].

2-Cyclization and multiple crosslinking reactions [6,7,33,51-53]: A kinetic scheme of free-radical crosslinking copolymerization of vinyl/divinyl monomers can be written as follows. The polymerization system involves three types of vinyl groups; those on vinyl and divinyl monomers and those on polymer chains, i.e., pendant vinyls. Accordingly, the polymerization can be considered as a special case of terpolymerization in which one of the vinyl groups (pendant vinyls) is created during the course of the reaction when the vinyl on the divinyl monomer reacts.

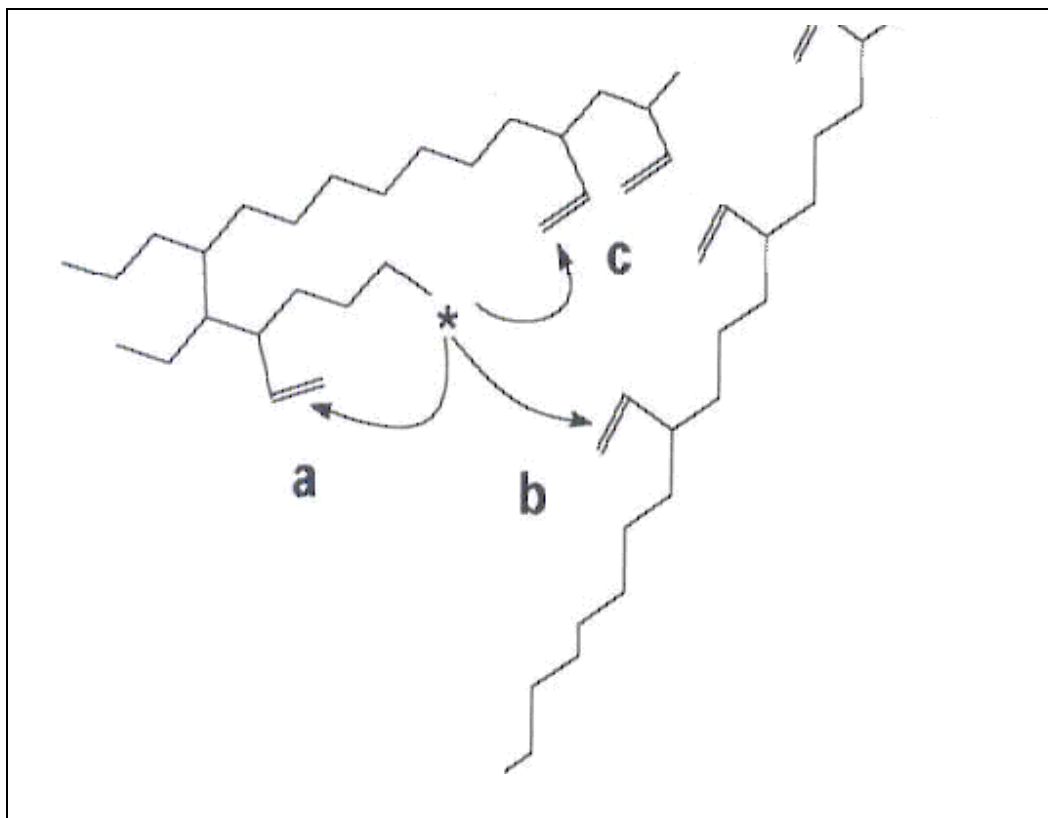


Figure 4.1: Schematic picture of cyclization (a), crosslinking (b) and multiple crosslinking (c) in free-radical crosslinking copolymerization.

The pendant vinyl groups thus formed can then react by cyclization, crosslinking, or multiple crosslinking reactions, or remain pendant (Figs. 4.1 and 4.2). With the cyclization the cycle is formed when the macroradical attacks the pendant vinyl groups in the same kinetic chain, while with multiple crosslinking it is formed if the radical attacks double bonds pendant on other chains already chemically connected with the growing radical (Fig. 4.1).

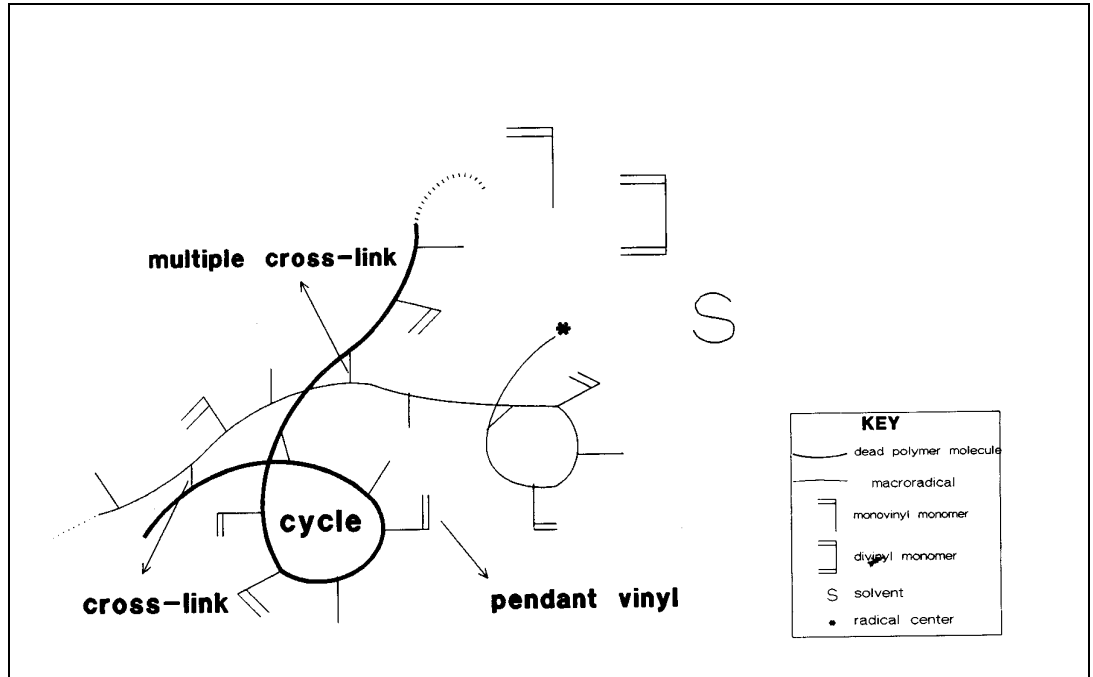


Figure 4.2: Schematic representation of the pre-gel period in free-radical crosslinking copolymerization.

The cyclization reactions predominate in the early stage of polymerization. The extent of these reactions increases as the dilution degree increases or as the crosslinker concentration increases. The cycles formed due to cyclization are elastically ineffective intramolecular links and therefore, they reduce the effective crosslink density of gels. The multiple crosslinking reactions form highly crosslinked regions of polymer networks. The regions, where the multiple crosslinks form, have a higher crosslink density than do others so that they increase the local crosslink density of gels (Fig.4.2).

As a result of the spatial gel inhomogeneity, highly crosslinked regions of a gel will not swell as much as the other regions. This leads to the concentration fluctuations in gel so that the gel scatters much more light than an equivalent semi-dilute polymer solution. The total scattering intensity from gels, $R_{\text{gel}}(q)$, can be written as a sum of the scattered intensity from a corresponding semi-dilute polymer solution, $R_{\text{soln}}(q)$, and that of the excess scattering, $R_{\text{ex}}(q)$ [3,8]:

$$R_{\text{gel}}(q) = R_{\text{soln}}(q) + R_{\text{ex}}(q) \quad (4.1)$$

Note that $R(q)$ represents the Rayleigh ratio and related to the scattering light intensity through the equation (3.1). $R_{\text{soln}}(q)$ is reflecting the thermal fluctuations. The excess scattering, $R_{\text{ex}}(q)$ should permit the characterization of the network inhomogeneity [8]. The excess scattering intensity from a gel sample depends on the fluctuations of refractive index in the sample and on the sizes of regions over which these fluctuations occur. Suitable parameters for characterizing the network inhomogeneities are the mean square fluctuations of refractive index, $\langle \eta^2 \rangle$ and the correlation length, ξ , over which these fluctuations occur.

To interpret light scattering from gels, several functional forms of excess scattering $R_{\text{ex}}(q)$ have been proposed empirically, i.e., Debye-Bueche [23,25,54-63], Guinier [3,8,17], and Ornstein-Zernike [3,8,17] function. For example, the excess scattering was given by the Debye-Bueche function as:

$$R_{\text{ex}}(q) = 2 \pi K_{\text{DB}} \langle \eta^2 \rangle \int \frac{\gamma(r) \sin(qr) r^2 dr}{qr} \quad (4.2)$$

where K_{DB} is the optical constant, $K_{\text{DB}} = 8\pi^2 n_o^2 / \lambda^4$, n_o is the refractive index of solvent, λ is the wavelength of the incident light in the medium and $\gamma(r)$ is the correlation function which is a number varying with the distance r . The correlation function $\gamma(r)$ is defined as [55]:

$$\gamma(r) = \langle \eta_1 \eta_2 \rangle_{\text{AV}} / \langle \eta^2 \rangle \quad (4.3)$$

The best method for explaining this expression is as follows: Consider two points 1 and 2 in an inhomogeneous medium situated at a distance r . Now take the product of the two fluctuations in the refractive index η_1 and η_2 , the first measured in the point 1 and the second in point 2. Following this, move the points 1 and 2 around in the inhomogeneous medium, always keeping their distance r fixed. In this way, we will obtain a large number of the values of the product $\eta_1 \eta_2$ and we can find the average value of this product indicated by the $\langle \eta_1 \eta_2 \rangle_{\text{AV}}$. If $r = 0$ we will have $\langle \eta_1 \eta_2 \rangle_{\text{AV}} = \langle \eta^2 \rangle$. For large values of r , the average product will be zero, since in this case η_1 and η_2 will vary quite independently.

The function $\gamma(r)$ can be obtained from Fourier inversion of $R_{ex}(q)$. For many systems $\gamma(r)$ is found to be an exponential function:

$$\gamma(r) = \exp(-r/\xi) \quad (4.4)$$

Where the correlation length ξ serves as a measure of the extension of the inhomogeneities. The larger ξ , the larger are the extension of the inhomogeneities. Substitution of eq. (4.4) into eq. (4.2) and integrating between $r = 0$ and $r = \infty$, one obtains:

$$R_{ex}(q) = \frac{4\pi K_{DB} \xi^3 \langle \eta^2 \rangle}{(1 + q^2 \xi^2)^2} \quad (4.5)$$

which is known as Debye–Bueche equation. According to eq. (4.5), $R_{ex}(q)^{-1/2}$ versus q^2 plots are linear, which are called Debye–Bueche plots. The slope and intercept of $R_{ex}(q)^{-1/2}$ vs. q^2 plot gives the extension of inhomogeneities, ξ and the mean square fluctuation of the refractive index, $\langle \eta^2 \rangle$. It is evident that $R_{ex}(q)$ depends upon both of these parameters so that, for example, at $q=0$, $R_{ex}(q)$ becomes:

$$R_{ex}(0) = 4\pi K_{DB} \xi^3 \langle \eta^2 \rangle \quad (4.6.a.)$$

The mean square refractive index fluctuations $\langle \eta^2 \rangle$ relate to the concentration fluctuations in gels arising from the crosslink density fluctuations $(\Delta M_c)^2$. A relationship between $\langle \eta^2 \rangle$ and $(\Delta M_c)^2$, can be derived as follows [56]. The refractive index of a gel, n , can be expressed as follows:

$$n = n_0 + (n_1 - n_0) \nu_2 \quad (4.7)$$

where n_0 and n_1 are the refractive indices of solvent and polymer, respectively. Let us consider two regions in a sample denoted by A and B. The refractive indices of these regions are:

$$(n)_A = n_0 + (n_1 - n_0)(\nu_2)_A \quad (4.8)$$

and

$$(n)_B = n_0 + (n_1 - n_0)(\nu_2)_B \quad (4.9)$$

where $(\nu_2)_A$ and $(\nu_2)_B$ are the polymer concentrations in these regions. From equations (4.8) and (4.9), the refractive index difference between the regions A and B can be as:

$$\Delta n = (n_A) - (n_B) = (n_1 - n_0)\Delta \nu_2 \quad (4.10)$$

where $\Delta \nu_2$ is the difference of polymer concentration between the regions A and B. Since there are infinite number of regions in gels with different refractive indices, the mean square refractive index fluctuations, $\langle \eta^2 \rangle$ of the Debye-Bueche theory is equal to:

$$\langle \eta^2 \rangle \cong \langle \Delta n^2 \rangle = (n_1 - n_0)^2 \langle \Delta \nu_2 \rangle^2 \quad (4.11)$$

On the other hand, for high degrees of gel swelling, the Flory-Rehner equation (equation (2.1)) reduces to:

$$\nu_2 = \left(\frac{\rho V_1 \nu_2^{2/3}}{\bar{M}_c (0.5 - \chi)} \right)^{3/5} \quad (4.12)$$

Taking the derivative of ν_2 with respect to (\bar{M}_c) in eq. (3.14), one obtains:

$$\frac{d\nu_2}{d\bar{M}_c} = \frac{-3}{5} \frac{\nu_2}{\bar{M}_c} \quad (4.13)$$

or:

$$\Delta \nu_2 = \frac{(3/5)\nu_2}{\bar{M}_c} \Delta \bar{M}_c \quad (4.14)$$

Combining equations (4.11) and (3.14) leads to:

$$\langle \eta^2 \rangle \cong \frac{9}{25} (n_1 - n_0)^2 \nu_2^2 \frac{\Delta \bar{M}_c^2}{\bar{M}_c^2} \quad (4.15)$$

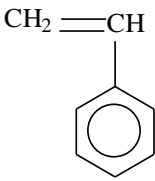
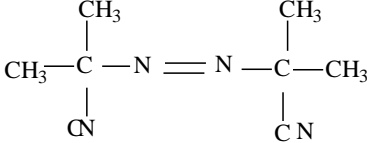
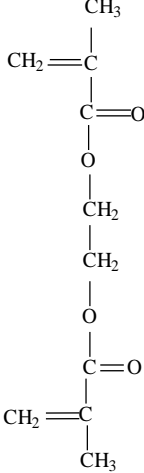
According to equation (4.15), $\langle \eta^2 \rangle$ parameter of the Debye-Bueche theory is directly related to the square of the fluctuations of the crosslink density, (ΔM_c^2) , i.e., to the spatial gel inhomogeneity.

5. EXPERIMENTAL

5.1 Materials

Styrene (Fluka) was freed from the inhibitor by shaking two times with 10 w/v % aqueous NaOH solution, washed three times with distilled water, dried over sodium sulfate, and finally distilled under vacuum at 40°C / 5mm Hg. 2,2' azobisisobutyronitrile (AIBN, Fluka) was recrystallized twice from methanol. HPLC-grade toluene (Riedel-de Haën) was used for the light scattering experiments while pure toluene (Riedel-de Haën) was used for the mechanical measurements. Ethylene glycol dimethacrylate (EGDM, Merck), HPLC-grade methanol (Riedel-de Haën) and carbon tetrachloride (CCl₄, Riedel-de Haën) were used without further purification. Table 5.1 shows the materials used in the preparation of polystyrene gel.

Table 5.1: Materials used in synthesis of polystyrene gels.

 <p>Styrene</p>	 <p>2,2' Azoisobutyronitrile (AIBN)</p>
 <p>Ethylene Glycol dimethacrylate (EGDM)</p>	<p>Carbon tetrachloride (CCl₄), Toluene and Methanol</p>

5.2 Synthesis of the Polystyrene gels

Polystyrene gels were prepared by free-radical crosslinking copolymerization of styrene and ethylene glycol dimethacrylate (EGDM) in toluene or toluene/methanol solutions at 60⁰ C in the presence of 2, 2' azobisisobutyronitrile (AIBN) as an initiator. A series of preliminary experiments were carried out to find the optimum condition for the gel formation. For this purpose, the initial monomer, the initiator, and the crosslinker (EGDM) concentrations were taken as the independent parameters. The gelation was succeeded in the presence of 0.3 % by weight AIBN, at 30 v/v % initial monomer concentration and above 2 mol %EGDM. The reaction time was set to one day.

Preliminary experiments showed that, if the initial monomer concentration is above 40 v/v %, the resulting polystyrene gels produce nonlinear scattering plots, that is, marked curvature appears in the Rayleigh ratio $R(q)$ versus scattering vector q plots. Similar results were also obtained for polystyrene solutions of concentration above 40 v/v %. In this high concentration regime, one may expect that, in addition to the concentration fluctuations, density fluctuations also play an important role in the scattering intensity, which is responsible for the curvature of the angular dependence of the Rayleigh ratios. Linear $R(q)$ versus q plots were obtained if the monomer concentration at the gel preparation is below 40 v/v %. Moreover, no gel formation was observed if the concentration is below 20 %. Therefore, polystyrene gels suitable for light scattering measurements can be best prepared at about 30 v/v % initial monomer concentration.

For the light scattering measurements, polystyrene solutions were prepared in the same way as the gels, but EGDM was not added to the initial monomer mixture. The synthesis of both gels and solutions was carried out in a dust-free environment.

Mainly four set of experiments were carried out. In the first set of experiments, the initial monomer concentration was varied between 20 and 53.2 % by volume while the EGDM content was fixed at 4.9 mol %.

In the second set of experiments, the initial monomer concentration was kept constant at 30 v/v % while the amount of the crosslinker EGDM was varied between 0 and 9.7 mol %.

In the third set, various amounts of carbon tetrachloride (CCl_4) was used as a chain transfer agent. Here, a series of gels was prepared at a fixed initial monomer concentration (38 v/v %) and EGDM content (4.9 mol %) while the amount of the chain transfer agent CCl_4 was varied between 0 and 0.17 mol/mol styrene.

In the last set of experiments, the gelation reactions were carried out in toluene-methanol mixtures. Methanol was used as a poor solvent in the range between 0 and 22 v/v %. In these experiments, the initial monomer concentration and the mol % EGDM were kept constant at 30.2 v/v % and 4.04 mol % respectively. Details for the preparation of the polystyrene gels at 30 v/v % initial monomer concentration and in the presence of 3.09 mol % EGDM are given in the following scheme:

AIBN (0.0163 g) was dissolved in toluene and then, styrene (5.7 ml), EGDM (0.3 ml) and toluene were added to give a total volume of 20 ml. To eliminate oxygen from the polymerization system nitrogen was bubbled through the solution for 15 min. For the light scattering measurements, the solutions were filtered directly into light scattering vials. For mechanical measurements the solutions were transferred to glass tubes of 5 mm internal diameter and 150 mm long. The glass tubes and the vials were placed in a thermostat at 60⁰ C and the polymerization was conducted 24 h.

5.3 Polymer Network Concentration at the State of the Gel Preparation

The presence of a solvent during the gel formation process is known to produce supercoiled polymer chains in the dry state so that the increase of their dimensions during swelling does not require much loss of their conformational entropy. As a result, the mechanical properties and the swelling behavior of gels sensitively depend on the degree of dilution at which they are formed. The degree of dilution of the networks after their preparation was denoted by ν_2^0 , the volume fraction of crosslinked polymer after the gel preparation. In order to determine ν_2^0 , the gels after preparation were first swollen in toluene over a period of at least two weeks until no further extractable polymer could be detected then dried at 80⁰C under vacuum to constant weight. ν_2^0 was calculated as:

$$v_2^o = \left[1 + \frac{(q_F - 1)\rho}{d_1} \right]^{-1} \quad (5.1)$$

where q_F is the mass swelling ratio after the gel preparation (mass of gel after preparation /mass of dry gel), ρ and d_1 are the densities of crosslinked polymer and solvent. [$d_1 = 0.867$ g/ml and $\rho = 1.05$ g/ml].

5.4 Swelling Measurements

The gels in the form of rods of 5 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of toluene at $24 \pm 0.5^\circ\text{C}$. In order to reach swelling equilibrium, the gels were immersed in toluene for at least two weeks replacing the toluene every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples by a calibrated digital compass (Mitutoyo, measuring range = 0-150 mm, accuracy = ± 0.002 mm). The equilibrium volume swelling ratio of the gel samples with respect to the after preparation state V/V_0 was calculated as:

$$\frac{V}{V_o} = \left(\frac{D}{D_o} \right)^3 \quad (5.2)$$

where D and D_0 are the diameters of gel sample after equilibrium swelling and after preparation, respectively. The volume swelling ratio with respect to the dry state of gels q_v was calculated as:

$$q_v = \frac{V/V_o}{v_2^o} \quad (5.3)$$

5.5 Mechanical Measurements

The mechanical measurements were conducted in a thermostated room of 24 ± 0.5 °C. Uniaxial compression measurements were performed on the polystyrene gels just after their preparation. The key parts of the apparatus used for measuring stress-strain data on the gels are shown in Figure 5.1.

Briefly, a cylindrical gel sample of 5 mm in diameter and 13 mm in length was placed on a digital balance. A load was transmitted vertically to the gel through a rod fitted with a PTFE end-plate. The force acting on the gel F was calculated from the reading of the balance m as:

$$F = mg \quad (5.4)$$

where g is the gravitational acceleration, (9.803 m/s^2). The resulting deformation $\Delta l = l_o - l$, where l_o and l are the initial undeformed and deformed lengths, respectively, was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm. The force and the resulting deformation were recorded after 20 s of relaxation. The measurements were conducted up to about 20% compression. The sample weight loss during the measurements due to toluene vaporization was found to be negligible. The deformation ratio α (deformed length/initial length) was calculated as:

$$\alpha = 1 - \frac{\Delta l}{l_o} \quad (5.5)$$

The corresponding stress f was calculated as:

$$f = F / A \quad (5.6)$$

where A , is the cross-sectional area of the specimen, i.e.,

$$A = \pi \left(\frac{D_o}{2} \right)^2 \quad (5.7)$$

As pointed out in the theoretical section, for uniaxial deformation, the statistical theories of rubber elasticity yield for Gaussian chains an equation of the form:

$$f = G(\alpha - \alpha^{-2}) \quad (5.8)$$

where G is the elastic modulus of the gel sample.

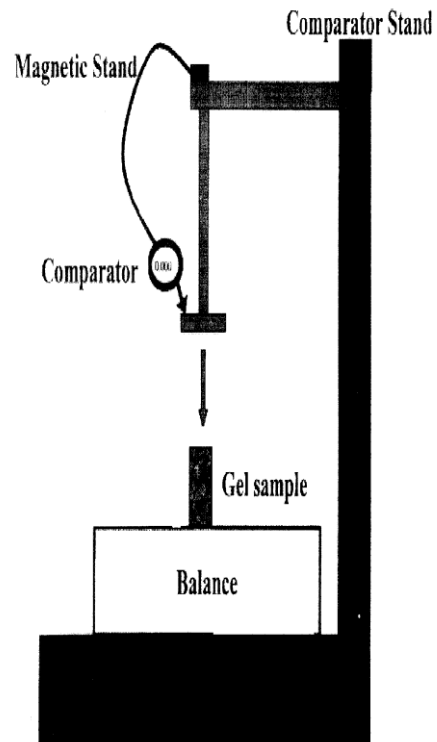


Figure 5.1: Uniaxial compression apparatus for measuring stress-strain data.

5.6 Light Scattering Measurements

5.6.1 Instrumentation

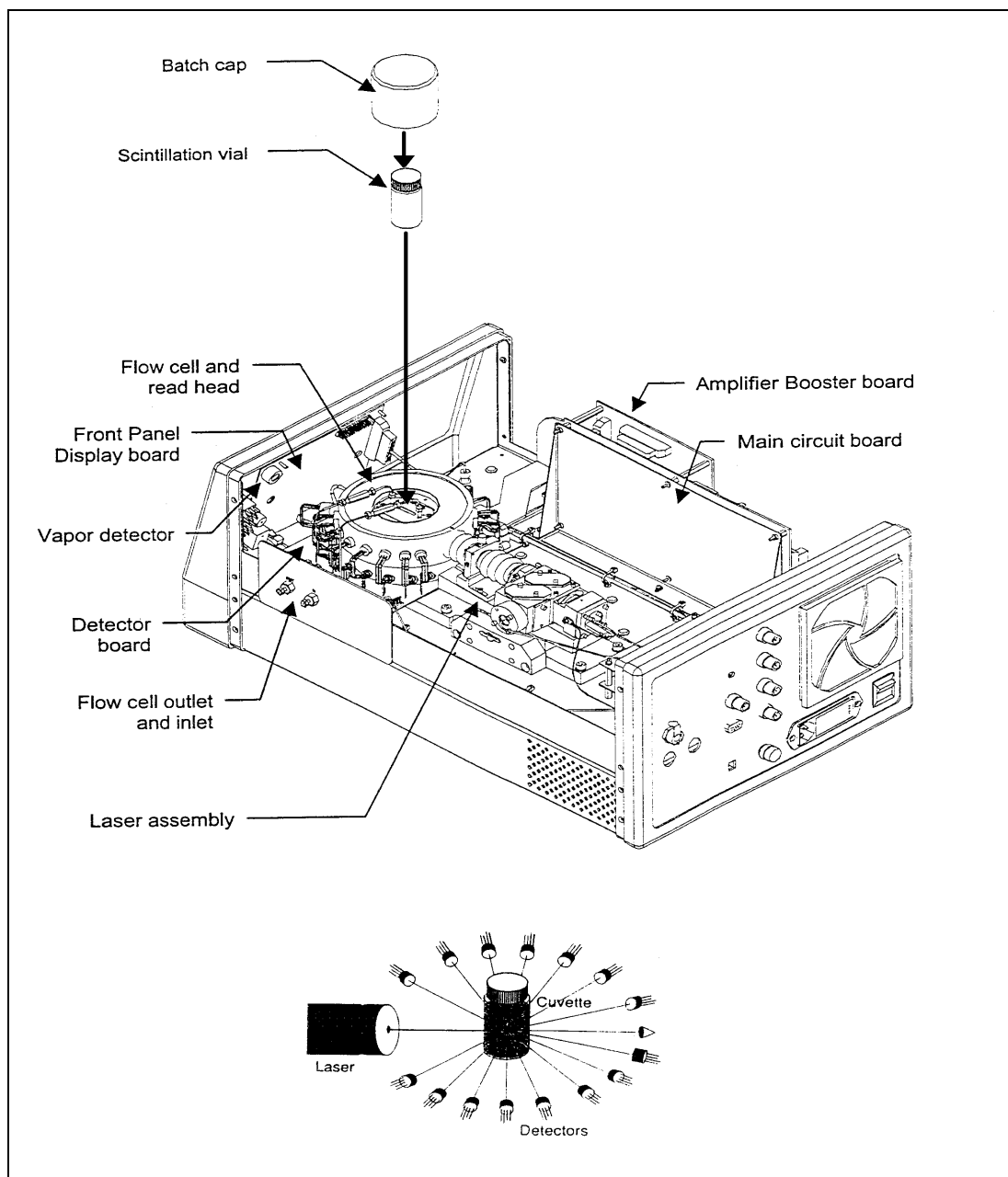


Figure 5.2: Schematic representation of the DAWN EOS for their macro-batch mode configuration.

The light scattering measurements were carried out at 24 ± 0.5 °C using a commercial multi-angle light scattering DAWN EOS apparatus (Wyatt

Technologies corporation) equipped with a vertically polarized 30 mV Gallium-arsenide laser operating at $\lambda=690$ nm and 18 simultaneously detected scattering angles (Fig.5.2). The 18 discrete photo-detectors spaced around the DAWN EOS Batch's in a unique multi-angle geometry, provide that the measurements can be made simultaneously over a broad range of scattering angles θ (between 19° and 149°). Dawn EOS works by sending laser light of wavelength 690 nm through sample and detecting scattering caused by molecules or impurities. The detectors convert the reading to an electrical impulse which is sent to a computer. When collecting the data from the instrument, periodically calibration, normalization and dark offset measurements were made to ensure accurate measurements.

1- Calibration: The instrument was calibrated to compute the calibration constant. The calibration measurements were made with great care as the accuracy of all other measurements depends upon them. Only the 90° detector was calibrated against a toluene standard. The other detectors were normalized with respect to the 90° detector during the normalization step. Toluene was used for calibration because it is a dust-free solvent and it has a relatively large, well known Rayleigh Ratio. HPLC-grade toluene filtered through $0.2\ \mu\text{m}$ filter was used for the calibration. During the calibration, the vial was rotated four times to obtain four constants. An average of these measurements was taken as the calibration constant.

2 Dark offset: Even without light, detectors pick up “noise”-small amounts of voltage inside the instrument. Dark offset measurements were made to record these identical voltages so that they can be subtracted from the light scattering data.

3 Solvent offset: Solvent offset measurements were made with filtered ($0.2\ \mu\text{m}$) HPLC-grade toluene. They were used in light scattering measurements on gels and to confirm the normalization process, described in next section. The cleanliness of the filtered solvent was checked by noting how much it scatters light at low angles than that at high angles.

4-Normalization: The photodiode detectors at all scattering angles other than 90° were normalized relative to the 90° detector using HPLC-grade filtered toluene.

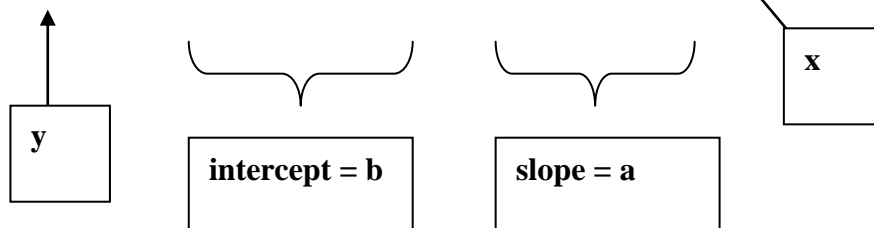
5.6.2 Light Scattering Experiments

For the light scattering measurements, the crosslinking polymerizations were carried out in the light scattering vials (a specified type of optical glass cylinders). The cleanliness of all the glassware was vital to eliminate the erroneous light scattering measurements. For this purpose, all glassware was rinsed in hot acetone prior using. The solutions were filtered through cellulose acetate membrane filters (pore size = 0.2 μm) directly into the vials. This process was carried out in a dust-free environment (TELSTAR laminar flow, 1800 m^3/h HEPA filter). All the gels subjected to light scattering measurements were clear and appeared homogenous to the eye. For the calculations of excess scattering from gels, all the crosslinking polymerizations were repeated under the same experimental conditions except that the crosslinker EGDM was not used. The gel samples were allowed to reach thermal equilibrium prior to the beginning of experiments.

The scattering light intensities from the instrument were recorded from $\theta = 19^\circ$ to 149° which correspond to the scattering vector q range $4.6 \cdot 10^{-4}$ to $2.6 \cdot 10^{-3} \text{ \AA}^{-1}$. During the measurements with the gel samples, the vial was rotated eight times between each cycle of data sampling to scan over a large number of different scattering volumes.

The excess scattering $R_{\text{ex}}(q)$ of the gel samples was determined by subtracting the scattering intensity of uncrosslinked samples $R_{\text{soln}}(q)$ from the scattering intensity of gels $R_{\text{gel}}(q)$, both having the same polymer concentration. Employing the Debye–Bueche analysis, the values of the mean square fluctuations of refractive index, $\langle \eta^2 \rangle$ and the correlation length, ξ were obtained by means of the linear regression of equation (4.5). Accordingly, when the inverse square of the excess scattering $(R_{\text{ex}}(q))^{-1/2}$ is plotted against q^2 , a straight line must be obtained (Debye-Bueche plot):

$$(R_{\text{ex}}(q))^{-1/2} = \left(2\sqrt{\pi K_{\text{DB}} \xi^3 \langle \eta^2 \rangle} \right)^{-1} + \frac{1}{2} \sqrt{\frac{\xi}{\pi K \langle \eta^2 \rangle}} q^2 \quad (5.9)$$



From the slope a and the intercept b of the Debye–Bueche plot, ξ and $\langle \eta^2 \rangle$ values were calculated as:

$$\xi = \sqrt{\frac{a}{b}} \quad (5.10)$$

and

$$\langle \eta^2 \rangle = (4\pi K a^{1.5} b^{0.5})^{-1} \quad (5.11)$$

In addition to the Debye–Bueche analysis of the light scattering data from gels, Ornstein-Zernike function:

$$R_{ex}(q) = \frac{R_{ex}(0)}{(1 + \xi_{OZ}^2 q^2)} \quad (5.12)$$

or Guinier function :

$$R_{ex}(q) = R_{ex}(0) \cdot \exp(-\xi_{GU}^2 q^2) \quad (5.13)$$

can also be used to interpret the light scattering data in terms of gel inhomogeneities. In these equations, $R_{ex}(0)$ is given by:

$$R_{ex}(0) = K \langle \eta^2 \rangle \xi^3 \quad (5.14)$$

where K being the optical constant $K = 32\pi^3 n^2 \lambda^{-4}$.

In addition to obtain characteristic network parameters ξ and $\langle \eta^2 \rangle$ by employing Debye–Bueche analysis, the Guinier (GU) and the Ornstein-Zernike (OZ) functions were also employed to the data. ξ and $\langle \eta^2 \rangle$ values were obtained by linear regressions of equations (5.12) and (5.13). In Table (5.2) the details of the Ornstein-Zernike and the Guinier analysis are collected, where the slope a and the intercept b correspond to each linear regression plot.

Table (5.2): The details of the Guinier and the Ornstein-Zernike analysis.

Ornstein-Zernike		Guinier
Linear regression	$\frac{1}{R_{ex}(q)} = \frac{1}{R_{ex}(0)} + \frac{\xi^2 q^2}{R_{ex}(0)}$	$\ln(R_{ex}(q)) = \ln R_{ex}(0) - \xi^2 q^2$
Plot	$\frac{1}{R_{ex}(q)}$ vs. q^2	$\ln(R_{ex}(q))$ vs. q^2
ξ	$= (a/b)^{1/2}$	$= (a)^{1/2}$
$\langle \eta^2 \rangle$	$= b^{1/2}/(Ka^{3/2})$	$= \exp(b)/(K a ^{3/2})$
$R_{ex}(0)$	$= 1/b$	$= \exp(b)$

According to Table 5.2 ξ and $\langle \eta^2 \rangle$ values calculated by GU, OZ and Debye-Bueche analysis relate each other by the following equations:

$$\xi_{OZ} \cong \xi_{GU} \cong \sqrt{2}\xi_{DB} \quad (5.15)$$

and

$$\langle \eta^2 \rangle_{OZ} \cong \langle \eta^2 \rangle_{GU} \cong 2^{-3/2} \langle \eta^2 \rangle_{DB} \quad (5.16)$$

Thus, ξ and $\langle \eta^2 \rangle$ values of the Guinier and Ornstein-Zernike functions were found to be approximately equal to those of the Debye–Bueche function.

6. RESULTS AND DISCUSSION

The aim of this work was to determine spatial network inhomogeneity in Polystyrene gels by use of static light scattering technique at a gel state just after preparation. We discuss the result of our experiments in three subsections. In the first subsection, the effect of crosslinker (EGDM) concentration on the gel inhomogeneity is discussed. The variation of the extent of gel inhomogeneity depending on the time of drying of polystyrene gels is also discussed in this section. In the second subsection, the effect of the presence of a chain transfer agent, namely CCl_4 , during the gel formation process on the gel inhomogeneity is discussed. In the last subsection, the quality of the polymerization solvent was varied and the resulting variations in the degree of gel inhomogeneity were investigated.

6.1 Effect of Crosslink Density

In this section, a series of polystyrene gels was prepared by free-radical crosslinking copolymerization in the presence of various amounts of EGDM as a crosslinker. In order to obtain polystyrene gels with different crosslink densities, EGDM concentration was varied between 3 and 7.9 mol %. The initial monomer concentration was fixed at 30 v/v %.

6.1.1 Effective Crosslink Density of Polystyrene Gels

The effective crosslink densities of polystyrene gels were estimated from the compression-strain tests carried out on gel samples just after their preparation. The characteristics of polystyrene gels are compiled in Table 6.1.

Table 6.1: The characteristic of polystyrene gels . V/V_0 = Normalized equilibrium volume swelling ratio (volume of swollen gel /volume of gel after preparation), ν_2^0 = volume fraction of the crosslinked polymer after gel preparation, G = elastic moduli of gels after their preparation, $\overline{M}_{c,chem}$ = the chemical value of \overline{M}_c , $\overline{M}_{c,eff}$ = the effective value of \overline{M}_c .

Mol % EGDM	V/V_0	ν_2^0	G (Pa)	$\overline{M}_{c,chem}$ (g/mol)	$\overline{M}_{c,eff} * 10^{-3}$ (g/mol)
3.7	2.6	0.1	1579	1410	160
4.7	1.9	0.11	3265	1100	86
5.8	1.6	0.13	5577	894	59
6.3	1.6	0.15	7246	824	52
7.9	1.2	0.15	11316	655	34

From the qF values, the volume fraction of the crosslinked polymer after the gel preparation ν_2^0 was calculated using eq. (5.1). The ν_2^0 values of gels are shown in column 3 of the Table. Assuming that the monomer conversion and the gel fractions are complete after the crosslinking, one may calculate the theoretical ν_2^0 value of polystyrene gels using the equation:

$$\nu_2^0 = 10^{-3} C_0 V_r \quad (6.1)$$

where V_r is the molar volume of polystyrene repeat units (99 ml/mol) and C_0 is the initial molar concentration of the monomers.

The theoretical value of ν_2^0 was calculated as 0.25. It is seen that the experimental ν_2^0 values listed in Table (6.1) are much smaller than the theoretical ones. This would indicate that the monomer conversions were not complete after the crosslinking copolymerization.

For a homogeneous affine network of Gaussian chains, the elastic modulus after the gel preparation G relates to the network crosslink density through the following equation:

$$G = \frac{\rho}{\overline{M}_c} RT v_2^0 \quad (6.2)$$

Using the experimental v_2^0 and G values of the gels listed in Table (6.1) together with eq. (6.2) the effective crosslink densities of the polystyrene gels in terms of $\overline{M}_{c,eff}$, the molecular weight of the network chains were calculated. For these calculations the following constants were used: $\rho = 1050 \text{ kg/m}^3$ $R = 8.314 \text{ J/Mole-K}$ and $T = 298 \text{ K}$. The values of $\overline{M}_{c,eff}$ are also shown in the Table. It is seen that $\overline{M}_{c,eff}$ decreases, i.e., the effective crosslink density increases as the EGDM concentration in the feed is increased. As a result, the swelling ratio V/V_0 decreases with increasing crosslinker content in the gels (Table 6.1).

If one assumes that all the EGDM molecules form effective crosslinks in the final network, the chemical value of $\overline{M}_{c,chem}$ can be calculated from the following equation:

$$\overline{M}_{c,chem} = \frac{Mr}{2X} \quad (6.3)$$

Where X is the crosslinker ratio (moles of EGDM/mole of monomer styrene) and M_r is the molecular weight of the polymer repeated unit (104 g / mol). The chemical values \overline{M}_c are also shown in the Table. It is seen that the chemical \overline{M}_c values are much smaller than the effective \overline{M}_c values. This indicates that a large fraction of EGDM was wasted by cyclization and multiple crosslinking reactions. The wasted EGDM fraction can be calculated using the following equation:

$$\text{Wasted EGDM \%} = \left(\frac{\overline{M}_{c,eff} - \overline{M}_{c,chem}}{\overline{M}_{c,eff}} \right) 10^2 \quad (6.4)$$

The calculations show that 98 to 99.5 % of EGDM used in the gel preparation were wasted, probably due to the cyclization and multiple crosslinking reactions.

6.1.2 Light Scattering Experiments

Light scattering measurements were carried out on polystyrene gels prepared at various crosslinker (EGDM) contents. The initial monomer concentration was 30 v/v %. The gels prepared above 9 mol % EGDM became first translucent and then opaque during the gel formation reactions. It is obvious that these gels have heterogeneities in a spatial scale of submicrometer to micrometer scale. Therefore, only gel samples with less than 9 % mol EGDM were subjected to light scattering measurements. An uncrosslinked polystyrene solution prepared at 30 v/v % initial monomer concentration was used as a reference for the calculation of the excess scattering of gels. In Fig.6.1A, the scattering light intensities of polystyrene gels $R_{\text{gel}}(q)$ and the corresponding polymer solution are plotted against the scattering vector q . In Fig.6.1B the excess scattering $R_{\text{ex}}(q)$ vs scattering vector q plots are shown. It is seen that gels scatter much more light than the corresponding polymer solution of the same concentration. The gel with 3.1 mol % EGDM shows very small increase in the scattered light intensity, values of which are comparable to the values obtained from polystyrene solution. A general observation is that even the presence of a small amount of the crosslinker EGDM increases drastically the scattering light intensity from the samples. At high EGDM contents, the scattering light intensity reaches values which are about 18 times larger than the intensities obtained from the solution of the uncrosslinked sample. Fig.6.1B shows that the excess scattering from gels increases with increasing amount of EGDM. Another interesting observation in Fig.6.1.B is that, at low EGDM content, the excess scattering is nearly q -independent. However, as the EGDM concentration is increased, the excess scattering becomes q dependent. The q dependence of $R(q)$ becomes more pronounced at high EGDM contents.

Since $R_{\text{ex}}(q)$ is a measure of the spatial inhomogeneity in a gel, the results shown in Figs. 6.1A and 6.1B indicate that more inhomogeneities are incorporated in the gel structure with increasing of EGDM content. To compare the excess scattering of different gels, we will focus on the scattering intensity measured at a fixed angle of 90° . Figure 6.2 shows the excess scattering at 90° $R_{\text{ex}}(90^\circ)$ plotted against the crosslinker (EGDM) content. $R_{\text{ex}}(90^\circ)$ increases first slightly up to about 6 mol % EGDM but then rapidly increases with a further increase in the EGDM

concentration. The vertical dotted line in Fig. 6.2 represents the critical EGDM concentration (8.5 mol %) at which the gels start to become opaque. The rapid increase in $R_{\text{ex}}(90^0)$ as the EGDM content approaches to the critical concentration suggests that the system phase separates during the gel formation process. As shown in the inset to Fig. 6.2, a good linear behavior was obtained if the data points are redrawn in a semi-logarithmic plot, indicating an exponential law between $R_{\text{ex}}(90^0)$ and EGDM mol %. This suggests the occurrence of a spinodal decomposition type phase separation in the gel samples as the crosslinker content is increased.

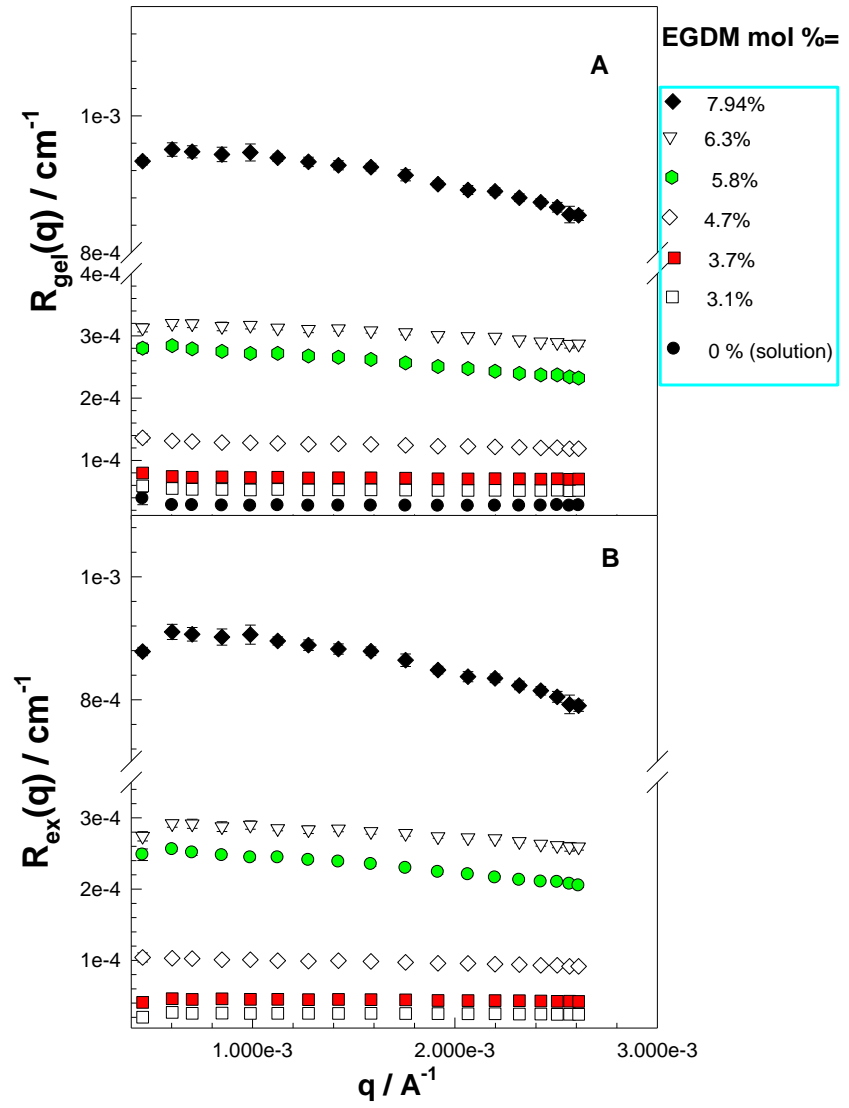


Figure 6.1: Scattering light intensities from gels $R_{\text{gel}}(q)$ (A) and the excess scattering $R_{\text{ex}}(q)$ (B) vs. scattering vector q plots for polystyrene gels of various crosslinker (EGDM) contents.

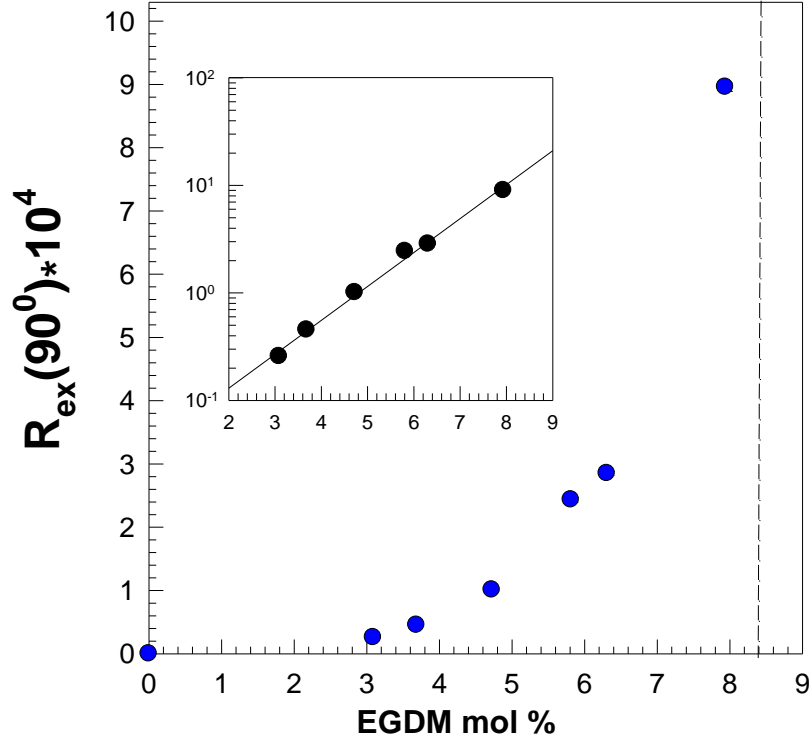


Figure 6.2: The excess scattering $R_{ex,q}$ measured at 90^0 ($R_{ex}(90^0)$) shown as a function of EGDM mol %. The inset to the Figure is a semi-logarithmic plot of the data points

In Fig. 6.3 the data points shown in Fig. 6.1 are replotted in the form of Debye-Bueche analysis (eq. (3.8)). It can be seen that perfectly straight lines are obtained in this type of analysis, indicating that the Debye-Bueche function works well. In fact, $\ln R_{ex}(q)$ vs q^2 and $R_{ex}(q)^{-1}$ vs q^2 plots also gave straight lines, implying that the Guinier and Ornstein-Zernicke functions also work well. From the slope and the intercept of the Debye-Bueche plots, the mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ and the correlation length of the scatterers ξ were obtained using equations (5.10) and (5.11), respectively.

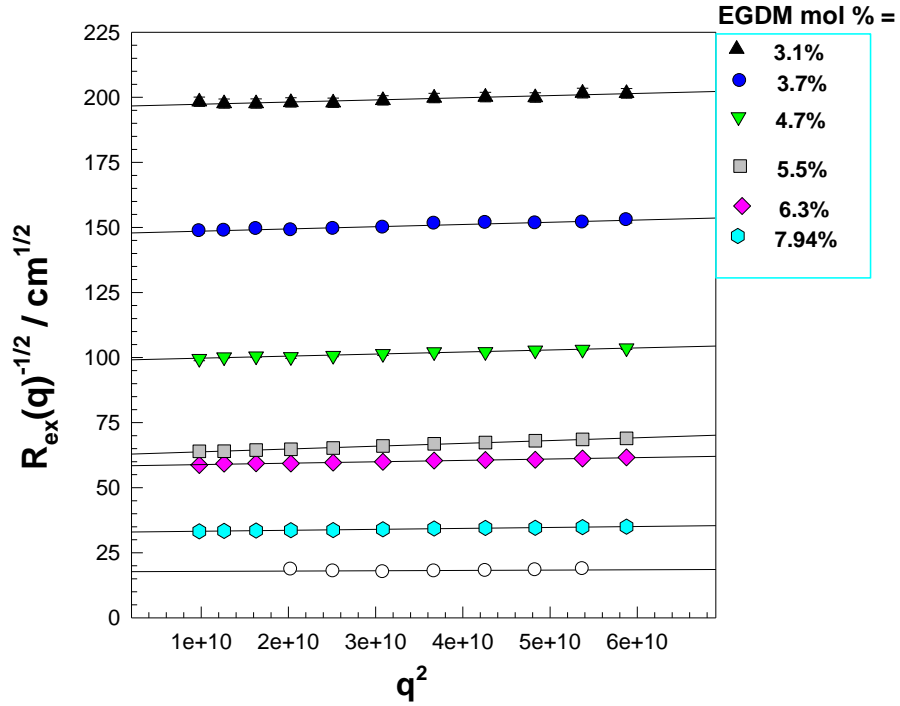


Figure 6.3: Debye-Bueche plots for polystyrene gels prepared at various EGDM mol %.

Calculations results of $\langle \eta^2 \rangle$ and ξ are collected in Fig. 6.4, plotted against the EGDM concentration. It is seen that the mean square fluctuations $\langle \eta^2 \rangle$ are in the range $10^{-7} - 10^{-5}$ and they increase with EGDM content. As shown in Fig.(6.4.B), the correlation length of the scatterers ξ was found to be 9 ± 2 nm and slightly increasing function of EGDM concentration. Thus, Debye-Bueche method shows that the correlation length, i.e., the extension of the inhomogeneities in polystyrene gels slightly increases while the extent of the fluctuations $\langle \eta^2 \rangle$ rapidly increases with increasing EGDM content.

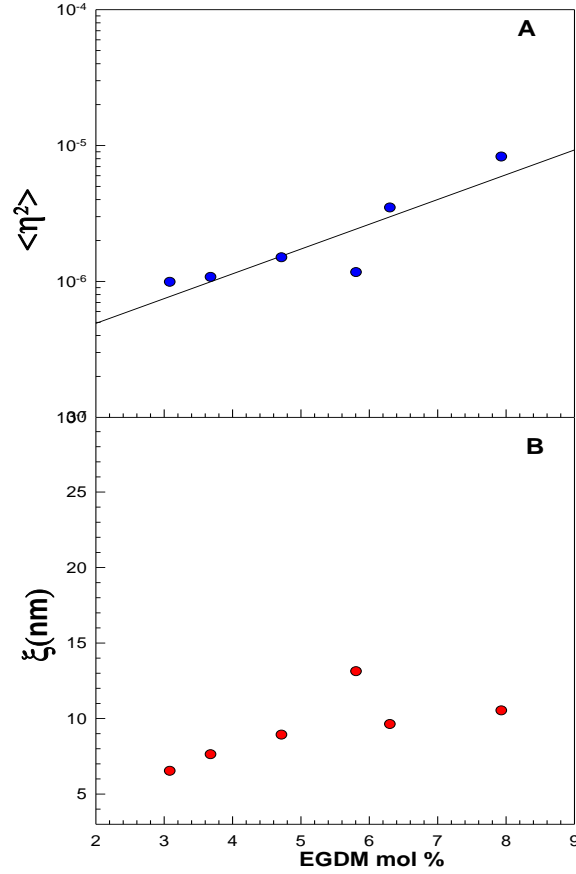


Figure 6.4: The mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ (**A**) and the correlation length of the scatterers ξ (**B**) in polystyrene gels shown as a function of EGDM mol %.

Combining the observations from Fig. (6.3) and Fig. (6.4.A), it has been established that the excess scattering $R_{\text{ex}}(q)$ and the mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ increase with rising EGDM content of polystyrene gels. Since both $R_{\text{ex}}(q)$ and $\langle \eta^2 \rangle$ are directly related to the concentration fluctuations in gels, i.e., to the spatial gel inhomogeneity, the results suggest that the degree of inhomogeneity in polystyrene gels increases with increasing EGDM content.

As pointed out in the previous section, cyclization and multiple crosslinking reactions are the main features of the gel formation processes by free-radical mechanism. At low crosslinker contents, since the local pendant vinyl group concentration surrounding the growing macroradical is relatively low, only a few multiple crosslinks is expected to occur after each crosslinking reaction.

Moreover, in the lightly crosslinked systems, the chains between crosslinks are long and relatively free to take up various positions throughout a rather large volume. As a result, they can minimize the effect of crosslink density distribution by moving from the regions of high crosslink density to regions of lower density. These would decrease the excess scattering and the mean square fluctuation of the refractive index. However, at high crosslinker contents, the possibility of multiple crosslinkages is enhanced due to the high pendant vinyl group concentration. Thus, in the highly crosslinked systems, the increased number of crosslinking points and relatively short network chains prevent such a homogenizing move. As seen in Table (6.1), the equilibrium swelling degree of the gels V/V_0 decreases from 2.7 to 1.6 with increasing amount of EGDM concentration. On the other hand, the elastic modulus of gels G increases as the amount of EGDM is increased (Table (6.1) and Fig. (6.6)). Thus, increasing crosslinker content increases the rates of both crosslinking and multiple crosslinking reactions. Since multiple crosslinks are elastically effective links in a small region of space, the regions, where the multiple crosslinks form, have a higher crosslink density than do others so that they will not swell as much as the other regions (Fig. 6.5). Thus, increasing extent of spatial gel inhomogeneity with increasing EGDM content of gels can be explained as a result of the enhancement of the multiple crosslinking reactions. Furthermore, an important finding of the present work is that there is a direct correlation between the scattering features of gels (Fig. 6.4) and their elastic properties (Fig. 6.5)

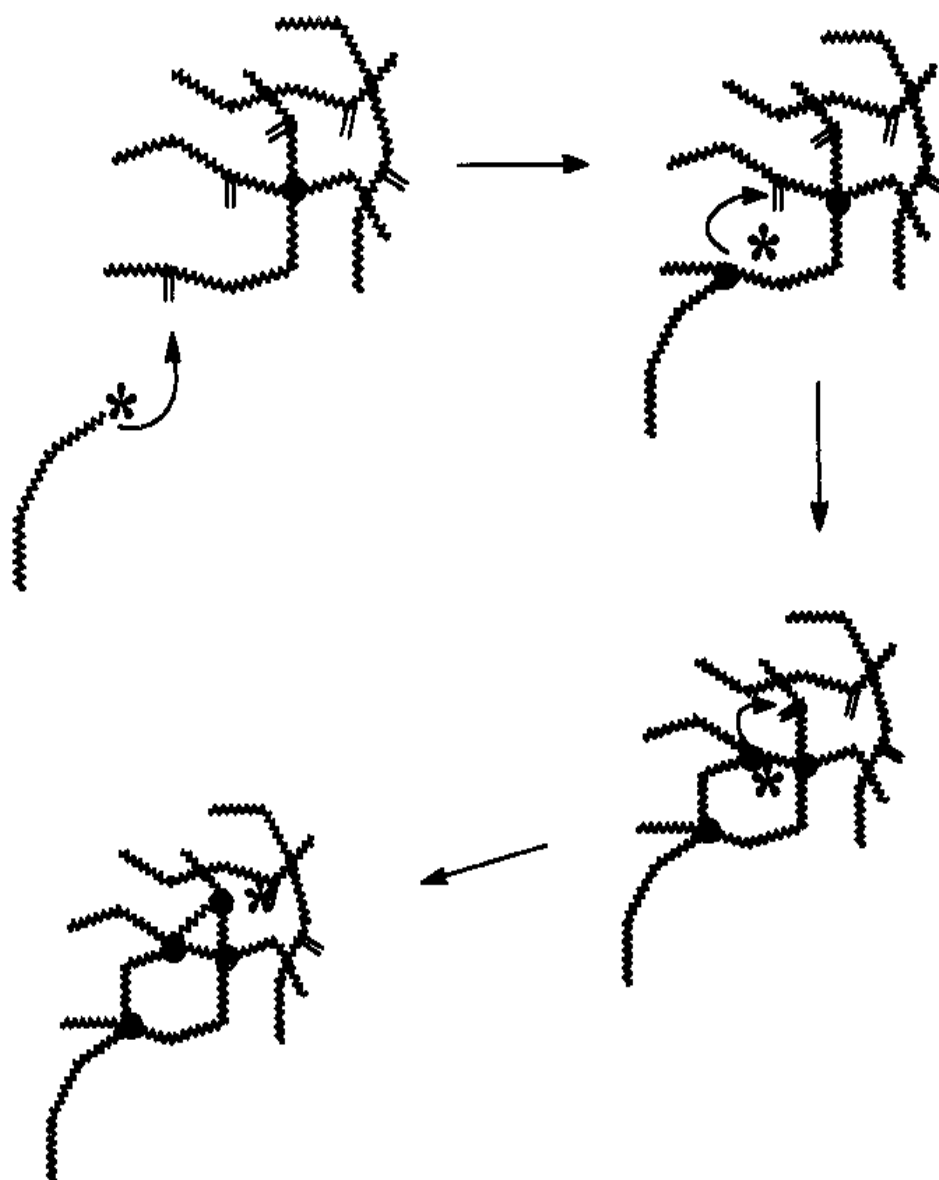


Figure 6.5: Schematic representation of multiple crosslinking reactions in free-radical crosslinking copolymerization. The regions, where the multiple crosslinks form, have a higher crosslink density than do others.

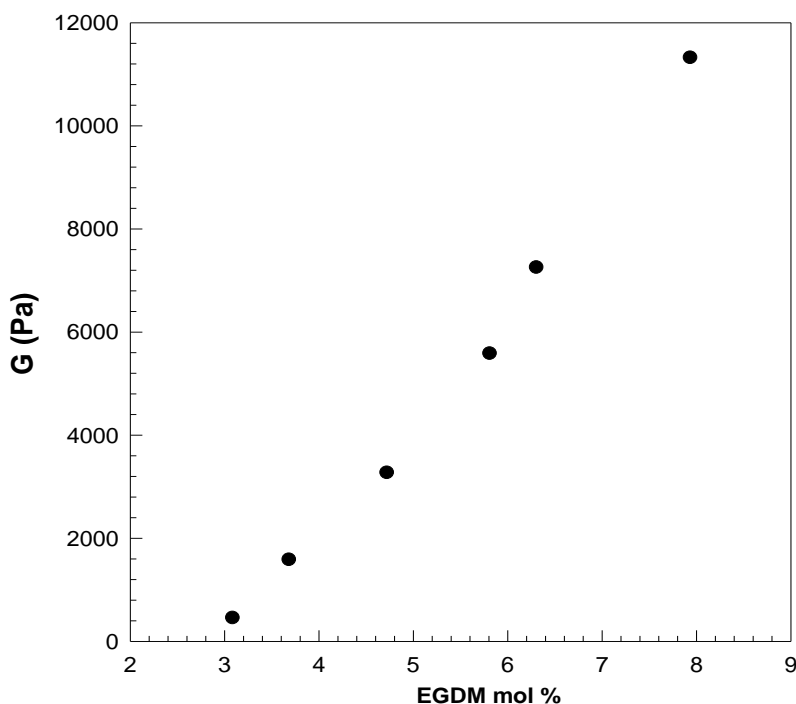


Figure 6.6: Variation of the elastic modulus of the polystyrene gels after preparation G with the mol % EGDM.

6.1.3 Effect of Drying of Polystyrene Gels Formed at Various Crosslinker Contents

In this part of our studies, polystyrene gels and the reference polystyrene solution were left in vials at room temperature to release their solvent (toluene) with time. During the experiments, all the gel and the solution samples kept their transparencies. Effect of drying of polystyrene gels with different crosslink densities on spatial inhomogeneity was monitored by static light scattering technique. Although, drying processes of the gels and the reference solution created some degree of nonuniformity in gels, the results will give an impression about the effect of drying on spatial inhomogeneity in polystyrene gels.

As pointed out in the previous section, an increase of the crosslinker content increases the possibility of the multiple crosslinking reactions which leads to the enhanced formation of highly crosslinked regions (clusters) in the final polystyrene gels. These highly crosslinked regions should shrink partly to ensure swelling

equilibrium. If this description is correct, the over scattering created by the increase in the crosslinker concentration should be suppressed by the partial drying of the gel. Fig. (6.7) shows $R_{ex}(q)$ vs. q plots for polystyrene gels at various drying times. The EGDM contents of gels are indicated in the Figure. It is seen that, for all the crosslinker contents studied, the excess scattering decreases with increasing drying time. Thus, the results collected in Fig. (6.7) support our idea that the over scattering can be suppressed by partially drying of gels. Since gel inhomogeneity is related to the concentration fluctuations, upon drying, the concentration difference between the dense and dilute regions is progressively reduced. This means that, when the gel dries, it becomes more homogeneous. To compare the different gels, in Fig. (6.8), the excess scattering intensities at $\theta = 90^\circ$ is plotted against the drying time. A striking observation in Fig. (6.8) is the fact that, there is a strong decrease in the excess scattering of the highly crosslinked gel as compared with less crosslinked one. This means that the homogenization of polystyrene gels during drying proceeds faster at high crosslinker contents due to the fact that the more shrunken dense regions can easily recover an almost random arrangement.

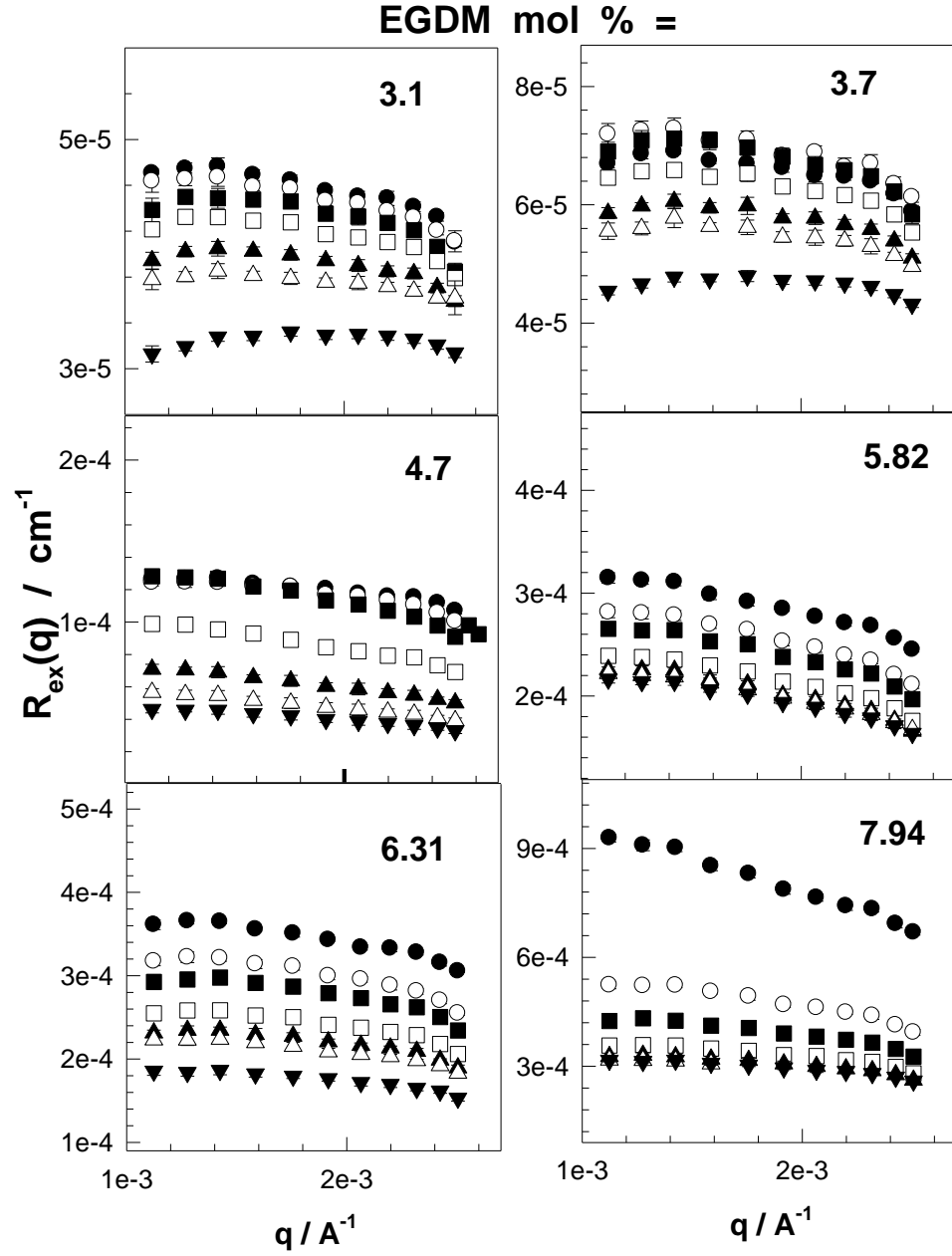


Figure 6.7: The excess scattering $R_{\text{ex}}(q)$ vs. scattering vector q plots for polystyrene gels at various EGDM mol % indicated in the Figure. The drying times are 18 (●), 36 (○), 50 (■), 71 (□), 85 (▲), 99 (△), and 110 days (▼)

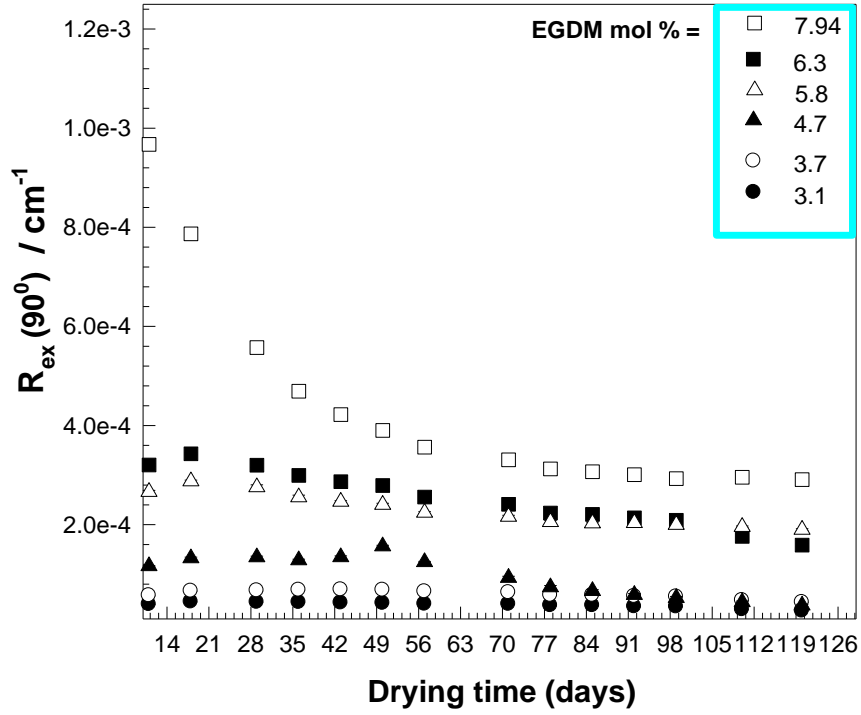


Figure 6.8: The excess scattering $R_{ex,q}$ at $q = 90^\circ$ ($R_{ex}(90^\circ)$) is plotted as a function of drying time for various EGDM %.

The scattered light intensities from partially dried gels were also interpreted using the Debye-Bueche analysis. As in the previous section, linear $R_{ex}(q)^{-1/2}$ vs. q^2 plots were obtained, from which the parameters $\langle \eta^2 \rangle$ and ξ were calculated using eq. (5.1). $\langle \eta^2 \rangle$ and ξ of gels are collected in Figure (6.9) plotted as a function of the drying time. It is seen that the size of the highly crosslinked regions ξ increases while the mean square fluctuations $\langle \eta^2 \rangle$ decrease with increasing time of drying. Since an inhomogeneous gel consists of regions of high and low polymer concentrations, this means that, upon drying, evaporation of the solvent reduces the concentration difference between regions. As a result, the size of the dense regions ξ increases while the extent of the concentration fluctuations $\langle \eta^2 \rangle$ decreases with increasing drying time.

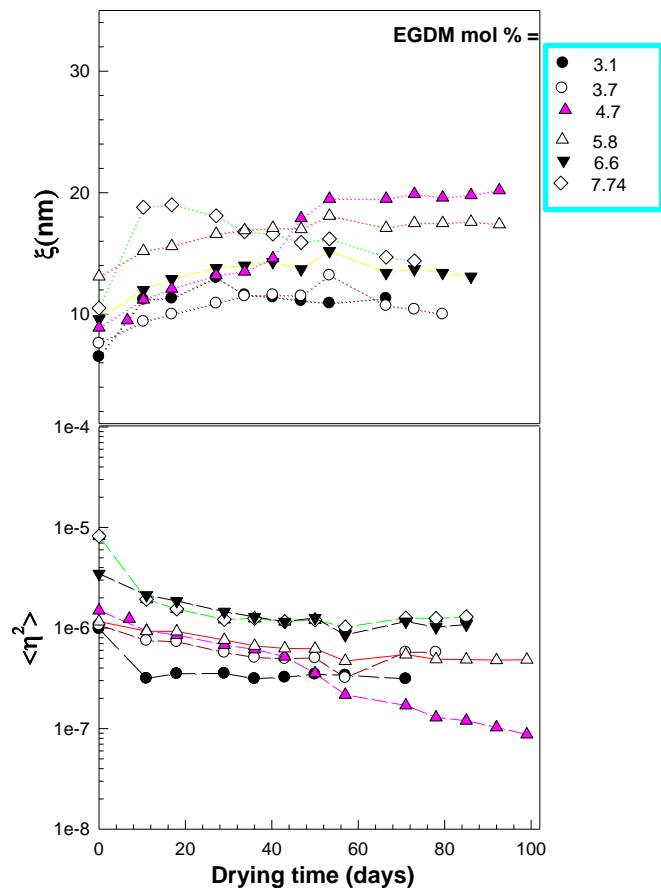


Figure (6.9): The mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ and the correlation length of the scatterers ξ in polystyrene gels shown as a function of the time of drying.

6.2 Effect of the Primary Chain Length

In this section, polystyrene gels and the corresponding polystyrene solutions were prepared in the presence of various concentration of carbon tetrachloride (CCl_4). CCl_4 is a well-known chain transfer agent and thus, addition of CCl_4 into the gel formation system will reduce the chain length of the primary molecules. The total monomer and the EGDM concentrations were fixed at 38 v/v % and 4.9 mol %, respectively. In this way, only the polymerization degree of the primary molecules was varied at a fixed pendant vinyl group concentration.

Figure (6.10) shows $R(q)$ versus the scattering vector q plots for polystyrene gels and the corresponding linear polystyrene solutions. CCl_4 concentrations were varied

between 0 and 0.1 mol CCl_4 / mol styrene and are indicated in the Figure. For polystyrene solutions, the light scattering intensity does not change much with the chain transfer agent (CTA) concentration; All the $R(q)$ vs. q plots for polymer solutions cross each other. However, the scattering light intensity from gels decreases continuously with the increasing CTA concentration. Even a small amount of CTA results in a decrease in the scattered light intensity from the gel sample. Furthermore, the scattering from the gel samples decreases drastically and becomes nearly q independent with increasing amount of CTA. At high CTA contents, the scattering light intensity reaches values which are about 2 times smaller than the intensity obtained from the sample without CTA. The results thus indicate that the addition of a chain transfer agent into the gel formation system reduces the extent of the spatial gel inhomogeneity.

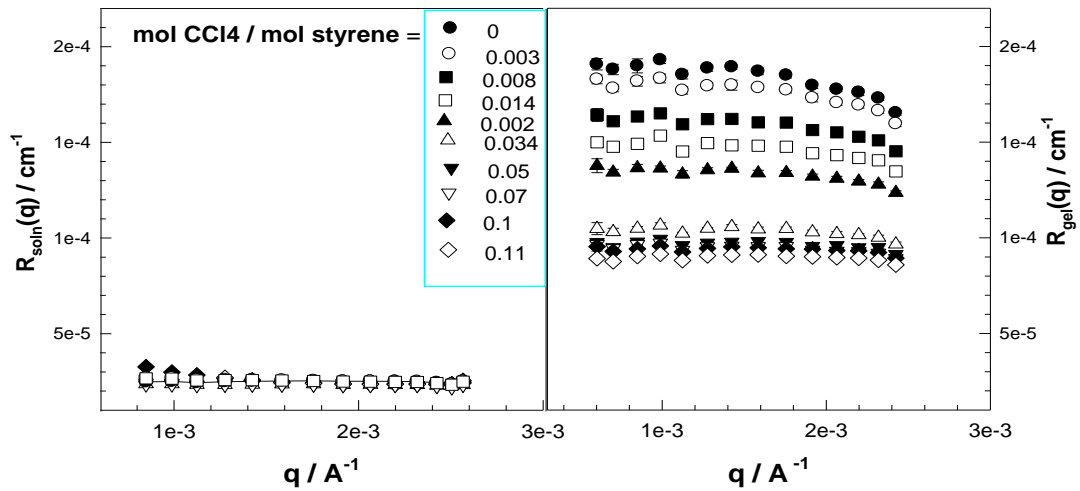


Figure (6.10): Scattering light intensities from gels $R_{\text{gel}}(q)$ and from solutions $R_{\text{soln}}(q)$ shown as a function of the scattering vector q for various CCl_4 contents.

In Figure (6.11), the scattering intensities from gels $R_{\text{gel},q}$ (filled circles), from solutions $R_{\text{soln},q}$ (open symbols) and the excess scattering $R_{\text{ex},q}$ (filled triangles), all measured at $\theta = 90^\circ$, are plotted against the chain transfer agent concentration. In polymer solutions, the scattered light $R_{\text{soln},q}$ increases only slightly with increasing concentration of CTA. However, $R_{\text{gel},q}$ and $R_{\text{ex},q}$ decrease first rapidly up to 0.03 mol CTA / mol styrene but then slightly as the amount of the CTA is further increased. At high CTA concentrations, the scattered light intensity from gel approaches to that

from the corresponding polymer solution. Thus, the results clearly demonstrate that the presence of CCl_4 as a chain transfer agent minimizes the degree of inhomogeneity in polystyrene gels.

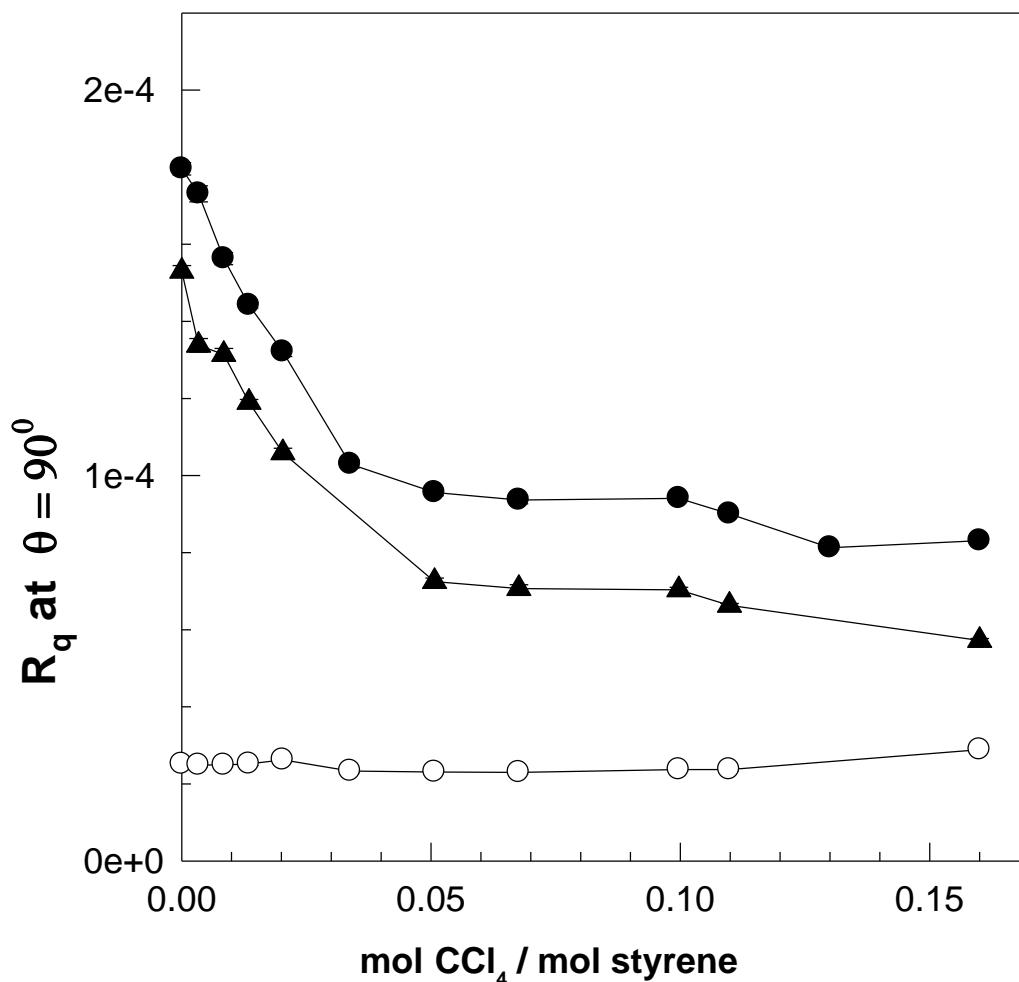


Figure (6.11): Scattering light intensities from gels $R_{\text{gel},q}$ (filled circles), from polystyrene solutions $R_{\text{soln},q}$ (open circles) and the excess scattering $R_{\text{ex},q}$ (filled triangles) measured at $\theta = 90^\circ$ shown as a function CCl_4 contents.

Elasticity tests were also carried out on gels prepared in the presence of various amount of CTA. In Figure (6.12), the elastic modulus of gels just after their preparation G is plotted against the CTA concentration. It is seen that, as the amount of CTA is increased, G decreases, i.e., the effective crosslink density of gels decreases. This result can be explained with decreasing chain length of the primary molecules as the CTA concentration is increased. As illustrated in Figure (6.13),

addition of CTA results in the formation of shorter primary molecules so that the number of chain ends and thus, the number of ineffective crosslink points at the end of the primary molecules increases. This necessarily reduces the elastic modulus of gels prepared in the presence of a chain transfer agent.

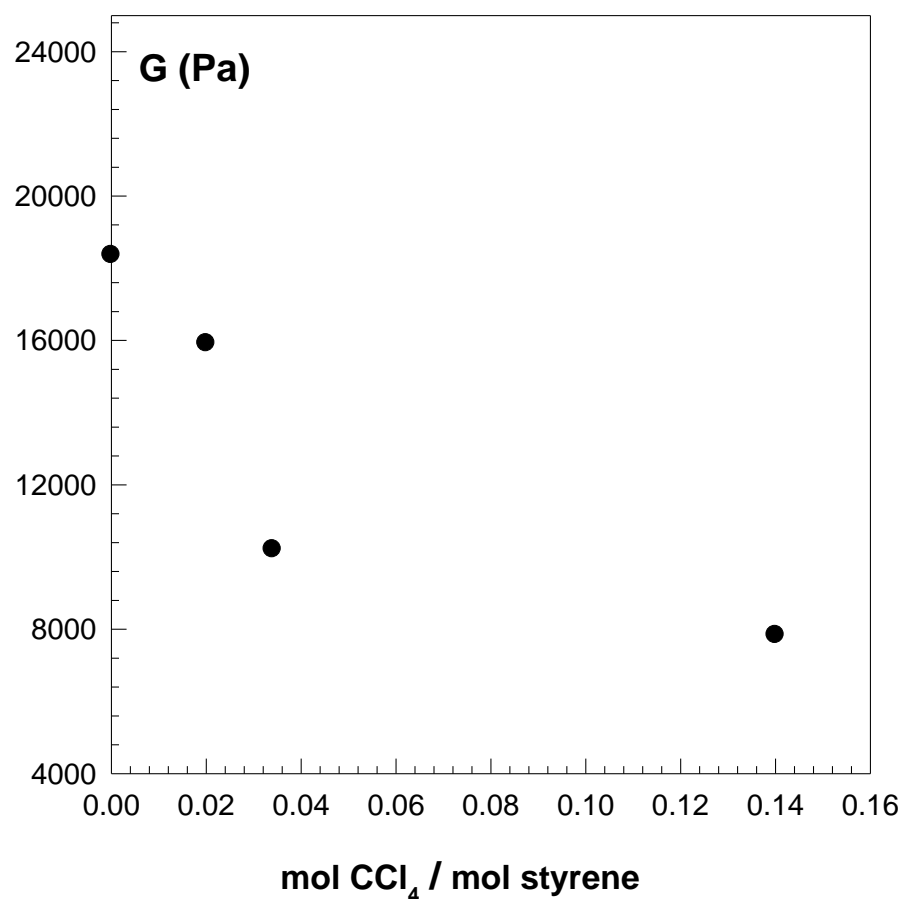


Figure (6.12): Variation of the elastic modulus of polystyrene gels with the amount of CCl_4 used in the gel preparation.

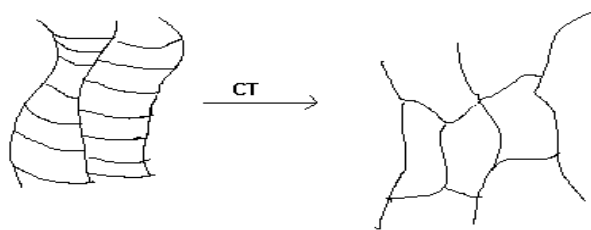


Figure (6.13): An effect of chain transfer agent on the crosslinked network structure. The chain transfer agent decreases the kinetic chain length and creates a network of shorter chains.

The reduction in the degree of the gel inhomogeneity in the presence of a chain transfer agent is a result of decreasing number of multiple crosslinking reactions. Since CTA produces shorter chains, increasing amount of CTA decreases the number of pendant vinyl groups on the individual molecules during the gel formation process so that the extent of multiple crosslinking reactions also decreases. Another point is that the extent of gel inhomogeneity is directly proportional to the elastic moduli of gels.

6.3 Effect of Solvent Quality

Research on the influence of solvent quality on polymerization has shown that the choice of solvent impact the polymerization in a variety of manner. Solvent quality affects the diffusion of the polymer chains, the viscosity of the polymerization medium, the intramolecular termination rate, the primary chain length, the gel point conversion, the reactivity ratios and the extent of cyclization and multiple crosslinking reactions [57]. The work described in this section focuses on how the solvent quality during the crosslinking copolymerization alters the spatial inhomogeneity of polystyrene gels. Using both the static light scattering and elastic moduli measurements, the effect of solvent quality on spatial network inhomogeneity was investigated. For this purpose, the crosslinking copolymerization of styrene and EGDM was carried out in toluene-methanol mixtures. Toluene and methanol were

chosen because toluene is a good solvent but methanol is a poor solvent for polystyrene. Thus, increasing amount of methanol in the solvent mixture will decrease the quality of the solvent. The volume fraction of methanol in the solvent mixture, denoted by x_{MOH} , was varied between 0 and 0.22. Initial monomer and EGDM concentrations were fixed at 30.2 v/v % and 4.04 mol %, respectively. In Figure (6.14), the elastic modulus G of gels after preparation is plotted against x_{MOH} . Increasing x_{MOH} , i.e., decreasing quality of the solvent used in the gel preparation increases the modulus of the resulting gels. This means that increasing number of effective crosslinks forms as the solvent quality is decreased.

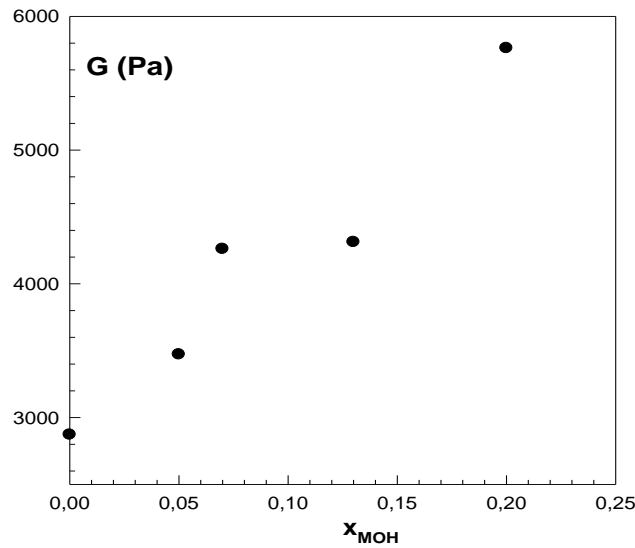


Figure (6.14): Variation of the elastic modulus of the polystyrene gels after preparation G with the volume fraction of methanol in the solvent mixture x_{MOH} used in the gel preparation.

Figure (6.15) shows the Rayleigh ratio vs. the scattering vector q plots for polystyrene gels $R_{\text{gel}}(q)$ and for the corresponding polystyrene solutions $R_{\text{soln}}(q)$. x_{MOH} values used in the gel and solution preparations are indicated in the Figure. It is seen that both gels and solutions, the light scattering intensities do not change much with the scattering vector q . Furthermore, scattered light intensities from polymer solutions $R_{\text{soln}}(q)$ and from gels $R_{\text{gel}}(q)$ increase with increasing volume fraction of methanol in the solvent mixture x_{MOH} . Another point shown in Fig. 6.15 is that the increase in $R_{\text{gel}}(q)$ with x_{MOH} is much more rapid than $R_{\text{soln}}(q)$. It must be noted that

methanol has a lower refractive index than toluene (1.3243 versus 1.4879 at $\lambda = 690$ nm) so that the addition of methanol in the solution necessarily increases the extent of refractive index fluctuations. Thus, the increase in $R_{\text{soln}}(q)$ with the methanol content x_{MOH} can be attributed to the variation of the refractive index of the solvent mixture. In order to eliminate this effect, the excess scattering intensities $R_{\text{ex}}(q)$ were calculated as the difference between $R_{\text{gel}}(q)$ and $R_{\text{soln}}(q)$. The results of calculations are shown in Fig. (6.16) plotted against the scattering vector q . It is seen that, as x_{MOH} is increased, $R_{\text{ex}}(q)$ also increases indicating that the extent of inhomogeneities in polystyrene gels increases with decreasing solvating power of the polymerization solvent.

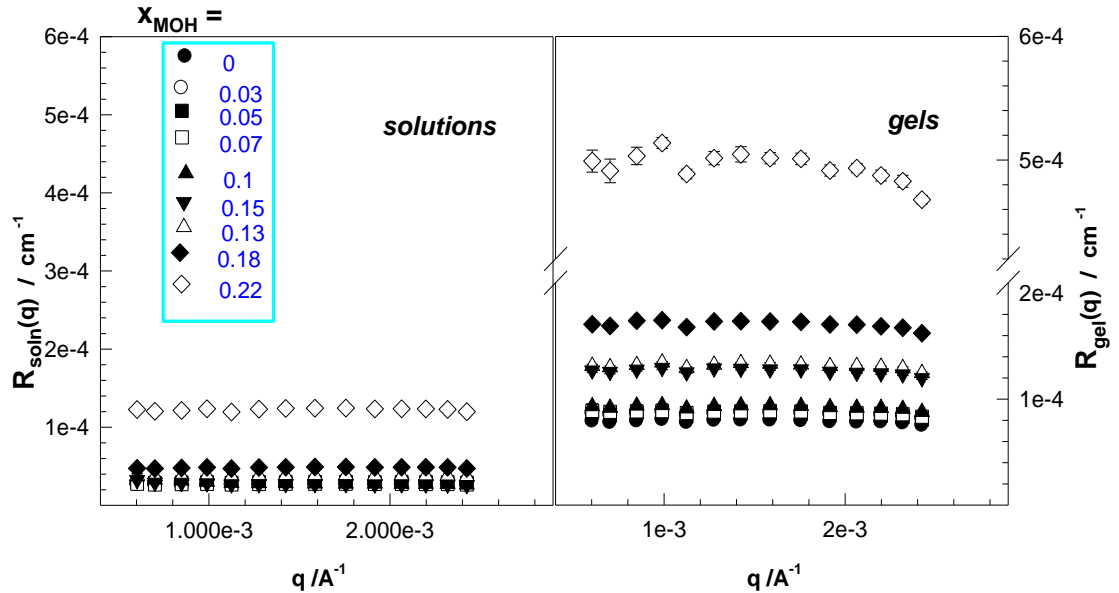


Figure (6.15): Scattering light intensities from gels $R_{\text{gel}}(q)$ and from solutions $R_{\text{soln}}(q)$ vs. scattering vector q plots. The gels and solutions were prepared in toluene/methanol mixture the volume fractions of methanol x_{MOH} are indicated in the Figure.

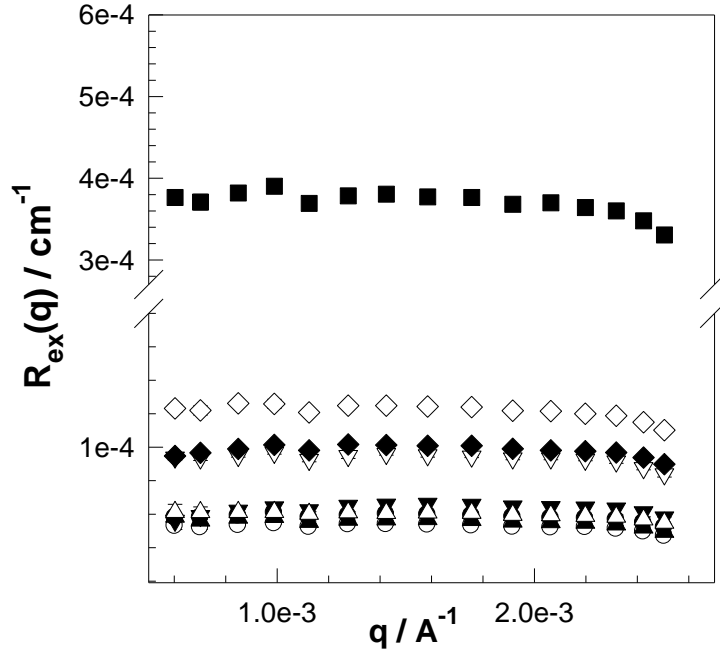


Figure (6.16): The excess $R_{\text{ex}}(q)$ and scattering vector q plots of gels prepared in toluene- methanol mixtures. $x_{\text{MOH}} = 0$ (\circ), 0.03 (\bullet), 0.05 (\blacktriangle), 0.07 (\triangle), 0.1 (\blacktriangledown), 0.13 (\triangledown), 0.15 (\blacklozenge), 0.18 (\diamond) and 0.22 (\blacksquare).

In Figure (6.17), $R_{\text{ex}}(\theta)$ values recorded at $\theta = 90^\circ$ ($R_{\text{ex}}(90^\circ)$) are plotted against the methanol concentration x_{MOH} . The increase in $R_{\text{ex}}(90^\circ)$ is first slight up to $x_{\text{MOH}} = 0.15$, but then it rapidly increases up to $x_{\text{MOH}} = 0.22$. Light scattering measurements were also interpreted in terms of Debye-Bueche plots, $\langle \eta^2 \rangle$ and ξ of the gel samples were calculated. The correlation length of scatterers ξ was found to be 8.6 ± 0.6 nm and slightly decreasing function of methanol concentration. The semi-logarithmic plot in Figure (6.18) showing methanol concentration dependence of the mean square fluctuations of the refractive index $\langle \eta^2 \rangle$ indicates that the extent of fluctuations $\langle \eta^2 \rangle$ increases with decreasing quality of the polymerization solvent.

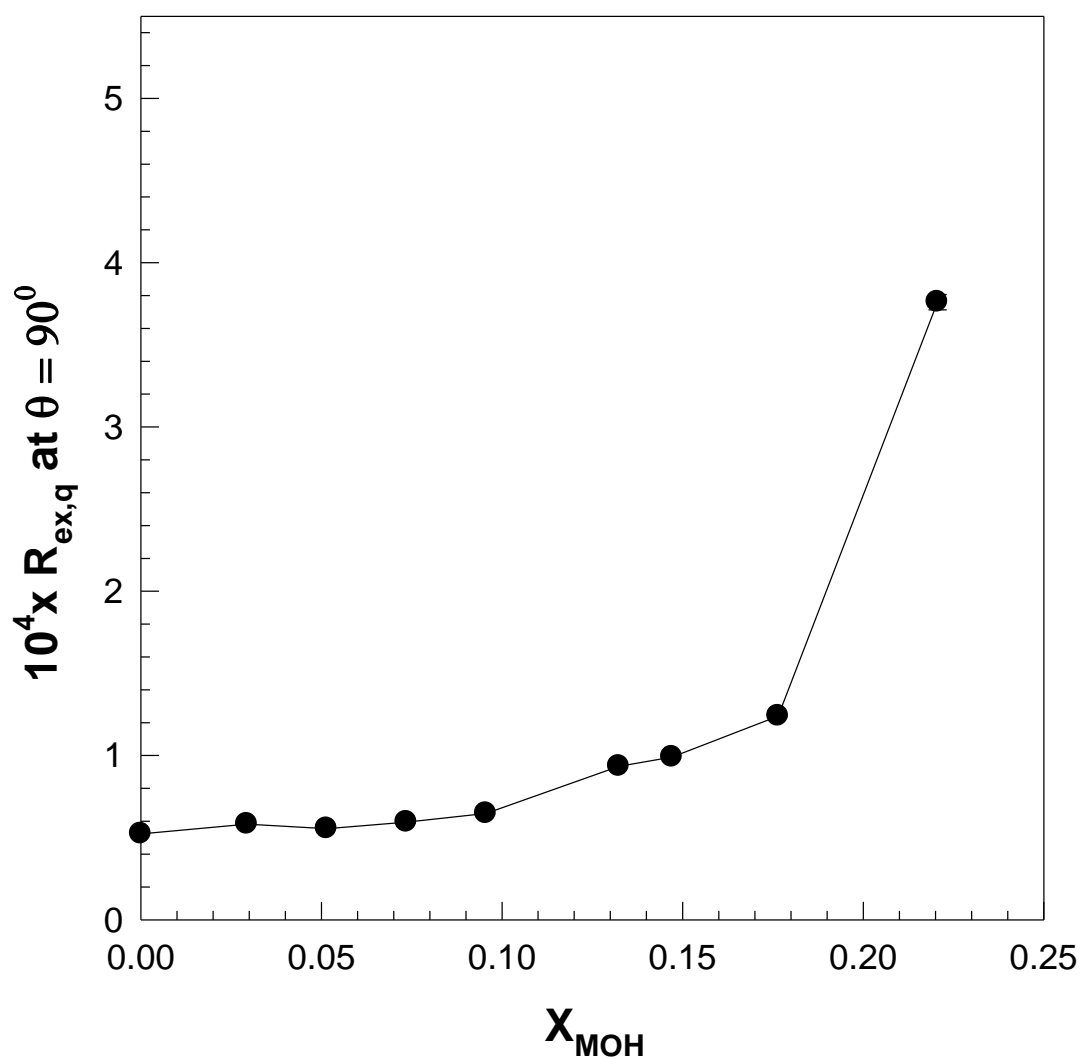


Figure (6.17): The excess scattering $R_{\text{ex},q}$ measured at $\theta = 90^\circ$ shown as a function of the methanol concentration x_{MOH} used in the gel preparation.

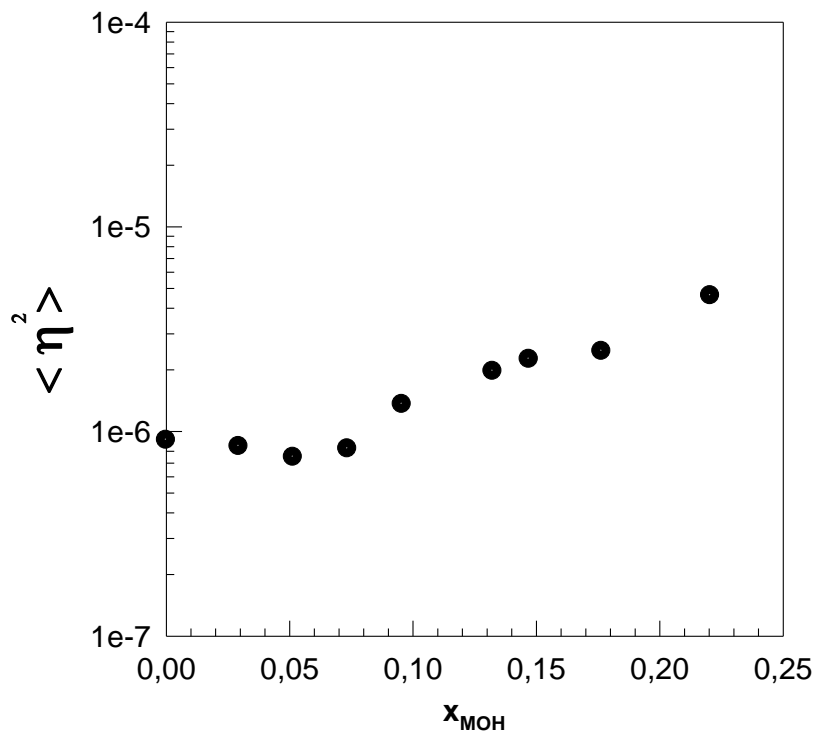


Figure (6.18): The mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ in polystyrene gels shown as a function of the methanol concentration x_{MOH} used in the gel preparation.

The results thus obtained can be explained with the following mechanism: If the polymer-solvent interaction is good during the crosslinking copolymerization, a pendant vinyl group will be found more difficult by radicals due to the thermodynamic excluded volume effect. Thus, the presence of larger polymer coils in the gel formation system will reduce the rates of the crosslinking and multiple crosslinking reactions (Fig. 6.19). In another case, if the polymer-solvent interactions are poor, the chains will coil more rather than stretch out, and the probability of crosslinking and multiple crosslinking is greater due to increased proximity of the pendant vinyl groups. According to this picture, a decrease in the solvent quality will increase both the elastic modulus G and the extent of spatial gel inhomogeneity, as was observed experimentally.

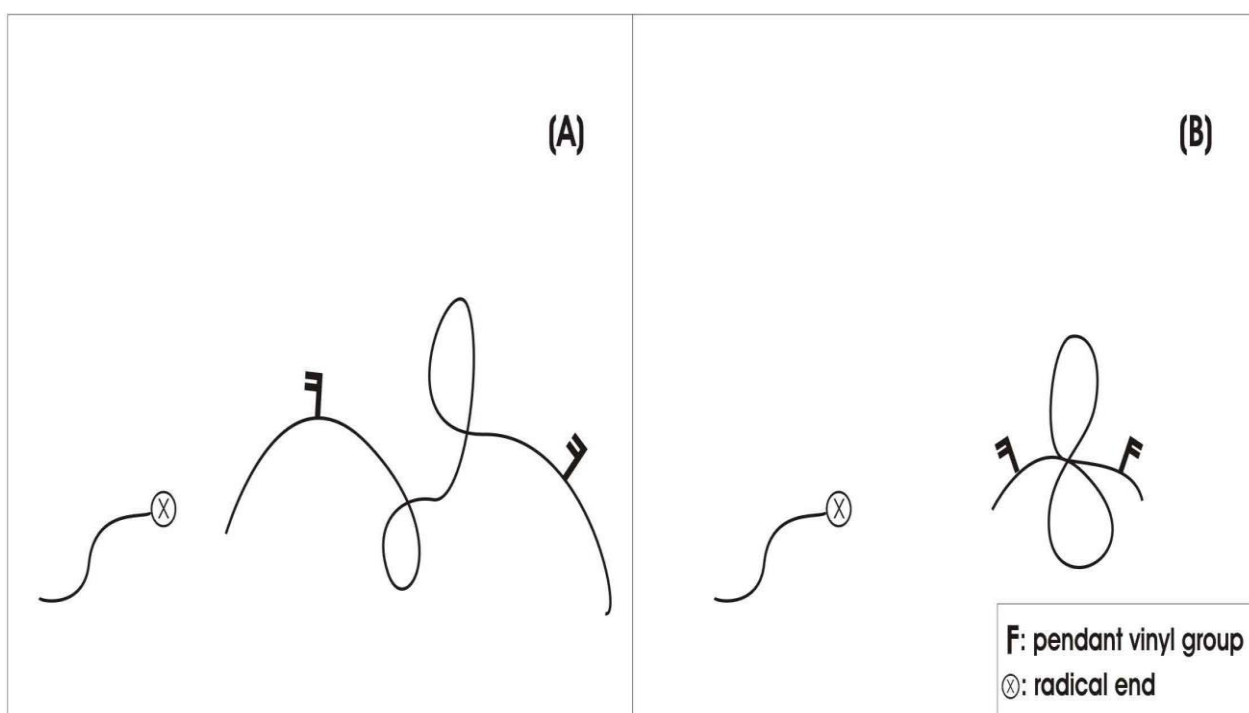


Fig. 6.19: Scheme of a growing radical in the presence of a polymer molecule (A) in a good solvent, and (B) in a poor solvent.

CONCLUSIONS

The extent of spatial inhomogeneity in polystyrene gels was investigated as a function of the gel synthesis parameters. The gels were prepared by free-radical crosslinking copolymerization of styrene and EGDM at 60⁰C using AIBN as the initiator. A chain transfer agent, namely carbon tetrachloride, was also included into the gel formation system at various amounts to find out the possible effect of the primary chain length on the gel inhomogeneity. Toluene-methanol mixtures of various compositions were used as the polymerization solvent. The experimental parameters varied were:

- a) the crosslinker (EGDM) concentration,
- b) the chain length of the primary molecules, and
- c) the quality of the polymerization solvent.

The gels were characterized by the swelling and elasticity tests as well as the static light scattering measurements at a gel state just after their preparation. The excess scattering from gels relating to the spatial gel inhomogeneity was determined by subtracting the scattering intensity of polystyrene solutions from the scattering intensity of polystyrene gels. Thus, semi-dilute polystyrene solutions having the same concentration as the gels served as a reference in understanding the extent of spatial gel inhomogeneities. The light scattering data were also analyzed within the framework of the Debye-Bueche theory. The following results were obtained:

- (1) The degree of spatial gel inhomogeneity increases with increasing crosslinker (EGDM) concentration. As the amount of EGDM in the comonomer feed is increased from 3 to 8 mol %, the mean square fluctuations in the gel $\langle \eta^2 \rangle$ increases from 10^{-7} to 10^{-5} while the correlation length ξ , that is the size of the highly

crosslinked regions in gel slightly decreases. The values of ξ were found to be in the range 9 ± 2 nm.

(2) As the polystyrene gels deswell, they become increasingly homogenous. As the time of drying is increased, the correlation length ξ increases while the mean square fluctuations $\langle \eta^2 \rangle$ decrease. Since an inhomogeneous gel consists of regions of high and low polymer concentrations, this means that, upon deswelling, evaporation of solvent reduces the concentration difference between the regions. The higher the crosslink density of gels, the faster the rate of the homogenization of gels.

(3) The degree of spatial gel inhomogeneity decreases with increasing amount of the chain transfer agent present in the gel formation process. Thus, decreasing chain length of the primary molecules results in the homogenization of gels.

(4) The degree of spatial inhomogeneity increases with decreasing quality of the polymerization solvent used in the gel preparation.

(5) A direct correlation was found between the elastic modulus of gels and the spatial gel inhomogeneity. Thus, gel synthesis parameters which are responsible for an increase in the elastic modulus of gels (increasing crosslinker concentration, decreasing chain transfer agent concentration or decreasing the solvent quality) also enhance of the extent inhomogeneities.

During the free-radical crosslinking copolymerization of styrene and EGDM, the distance between the pendant vinyl groups locating on the same molecule varies depending on the synthesis parameters. As illustrated schematically in Figure (7.1), decreasing crosslinker concentration (A), increasing chain transfer agent concentration (B), or increasing the quality of the polymerization solvent (C) increase the distance between adjacent pendant vinyl unsaturations.

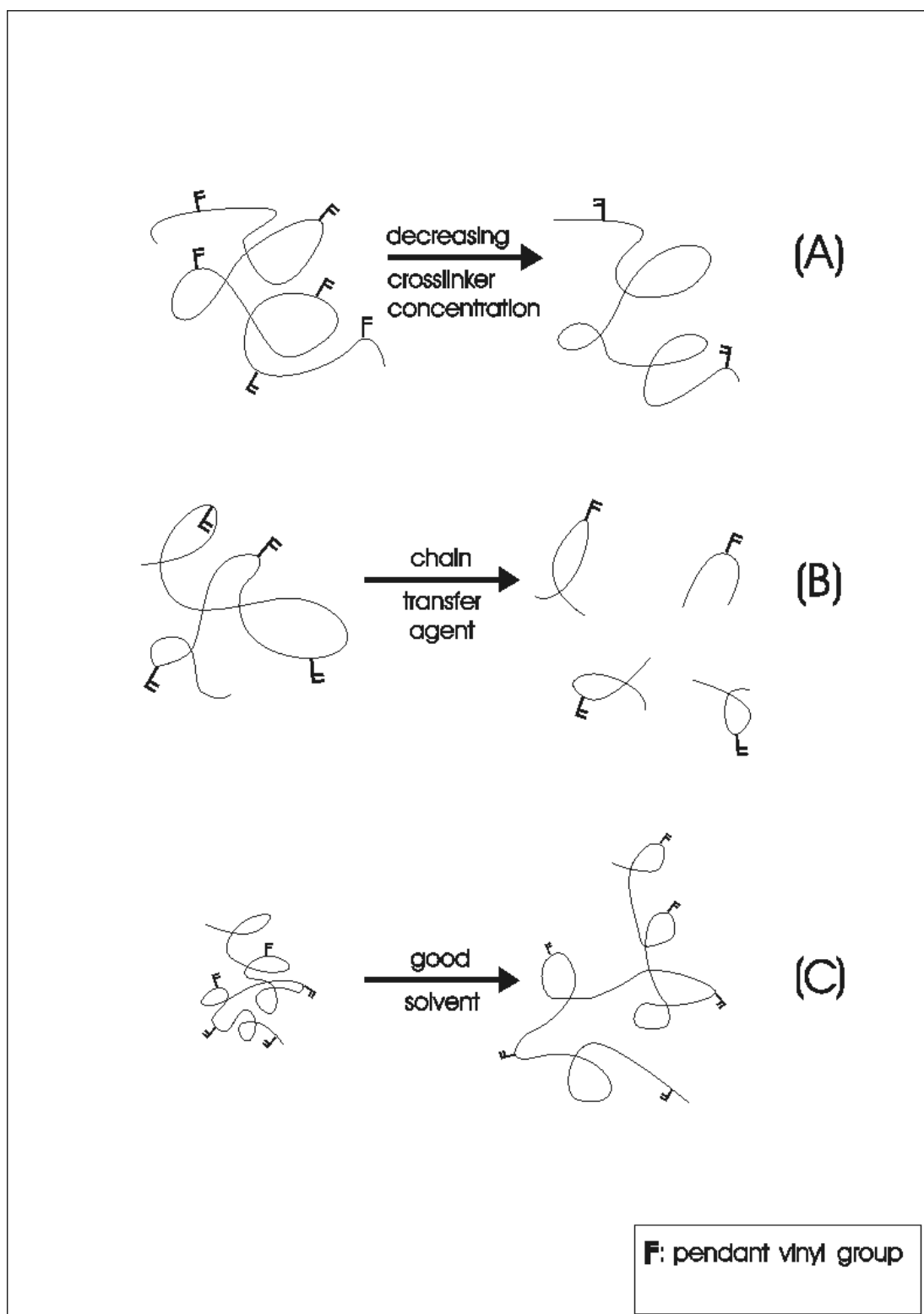


Figure 7.1: Effect of the gel synthesis parameters on the distance between the pendant vinyl groups locating on the same molecule.

As the distance between pendant vinyl groups in the gel formation system increases, the number of multiple crosslinking necessarily decreases so that the gels formed become increasingly homogenous. Thus, the experimental findings suggest that the factors increasing the distance between the pendant vinyl groups decrease the number of multiple crosslinks so that the degree of the spatial gel inhomogeneity also decreases. In concluding, in order to obtain gels with a minimum degree of spatial gel inhomogeneity, one should reduce the effective crosslink density of gels by (a) decreasing the crosslinker concentration, (b) adding a chain transfer agent in the gel formation system, or (c) using a good solvent as the medium of the crosslinking copolymerization.

REFERENCES:

- [1] **Tanaka, T.**, 1981. *Sci. Am.*, **244**, 110.
- [2] **Tanaka, T.**, 2000. *Experimental Methods in Polymer Science*, Chapter VI, Academic Press, Boston.
- [3] **Shibayama, M.**, 1998. *Macromol. Chem. Phys.*, **199**, 1.
- [4] **Takata, S., Norisuye, T., Shibayama, M.**, 2002. *Macromolecules*, **35**, 4779.
- [5] **Lindemann, B., Schröder, U. P., Oppermann, W.**, 1997. *Macromolecules*, **30**, 4073.
- [6] **Funke, W., Okay, O., Joos-Muller, B.**, 1998. *Adv. Polym. Sci.*, **136**, 139.
- [7] **Okay, O.**, 2000. *Prog. Polym. Sci.*, **25**, 711.
- [8] **Bastide, J., Candau, S. J.** In: *Physical properties of polymeric gels*, ed.: Cohen Addad, J.P., Wiley, 1996, p. 143.
- [9] **Zeldovic, K.B.; Khokhlov A.R.**; 1999. *Macromolecules* **32**,3488.
- [10] **Mallam, S., Horkay, F., Hecht, A. M., Geissler, E.**, 1989. *Macromolecules*, **22**, 3356
- [11] **Ikkai, F., Shibayama, M.**, 1997. *Phys. Rev. E*, **56**, R51
- [12] **Cohen, Y., Ramon, O., Kopelman, I. J., Mizraki, S.**, 1992. *J. Polym. Sci. Polym. Phys. Ed.*, **30**, 1055
- [13] **Schosseler, F., Skouri, R., Munch, J.P., Candau, S.**, 1994. *J. J. Phys. II*, **4**, 1221
- [14] **Shibayama, M., Tanaka, T., Han, C. C. J.**, 1992. *Chem. Phys.*, **97**, 6842.
- [15] **Horkay, F., McKenna, G. B., Deschamps, P., Geissler, E.**, 2000. *Macromolecules*, **33**, 5215
- [16] **Shibayama, M., Ikkai, F., Nomura, S.**, 1994. *Macromolecules*, **27**, 6383
- [17] **Shibayama, M., Ikkai, F., Shiwa, Y., Rabin, Y.**, 1994. *J. Chem. Phys.* 1997, **107**, 5227
- [18] **Ikkai, F., Iritani, O., Shibayama, M., Han, C. C.**, 1998. *Macromolecules*, **31**, 8526
- [19] **Hecht, A. M., Duplessix, R., Geissler, E.**, 1985. *Macromolecules*, **18**, 2167
- [20] **Bastide, J., Mendes Jr., E.**, 1990. *Makromol. Chem. Macromol. Symp.*, **40**, 81.
- [21] **Moussaid, A., Candau, S. J., Joosten, J. G. H.**, 1994. *Macromolecules*, **27**, 2102.
- [22] **Treloar, L.R.G.**, (1975). *The Physics of Rubber Elasticity*, University Press, Oxford.
- [23] **Soni, V. K., Stein, R. S.**, 1990. *Macromolecules*, **23**, 5257.
- [24] **Travas-Sejdic, J.; Easteal** ,2000. *Polymer* **41**,2535.
- [25] **Bueche, F.**, (1970). *J Colloid Interface* **33**:61.
- [26] **Shibiyama M., Morimoto, M., Namura, S.**, 1994. *Macromolecules*, **27**, 5060.
- [27] **Shibiyama M.,Fujikiwa Y., Namura, S.**, 1996. *Macromolecules*, **29**,6535.
- [28] **Wu, C., Zuo,J.,Chu, B.**,1989. *Macromolecules* **22**,633.
- [29] **Wu, C., Zuo,J.,Chu, B.**,1989. *Macromolecules* **22**,838.
- [30] **Wu, C., Zuo,J.,Chu, B., Steel G.**, 1989. *Macromol. Chem., Macromol. Symp.*, **45**,75.
- [31] **Bastide, J.,Leibler, L.**1980. *Macromolecules* **21**,2649.
- [32] **Baselga, J., Llorente M.A., Herenandez-Fuentes, I., Pierolla IF** (1989). *Eur. Polym. J.* **25**, 471.
- [33] **Naghash, H.J., Okay. O.**, 1996. *J Appl Polym Sci* **60**,971.

- [34] **Tobita, H., Hamielec A.E.**, 1990. *Polymer* **31**,1546.
- [35] **Flory, P.J.** (1953). *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press.
- [36] **Erman, B., Mark J.E.**, 1988. *Rubberlike Elasticity a Molecular Primer*, University Press, Canada.
- [37] **Bohren, F.C., Huffman, R.D.**, 1988. *Absorption and Scattering of Light by Small Particles*, Wiley-Interscience Press.
- [38] **Rayleigh, L.**, 1912. *The Scientific Papers of Lord Rayleigh vols.1-4*, Cambridge University Press, New York,
- [39] **Kara, S., Pekcan, Ö.**, 2001. *J. of Applied Polym. Sci.* **80**,823.
- [40] **Wyatt, P.J.**, 1993. *Analytica Chimica Acta.* **27**,1.
- [41] **Wu, C., Chu. B.**, 2000. *Experimental Methods in Polymer Science*, Academic Press, New York.
- [42] **Chu. B.**, 1991. *Laser Light Scattering*, 2nd ed., Academic Press, New York.
- [43] **Huglin. M.B.**, 1972. *Light Scattering from Polymer Solution*, Academic Press, New York.
- [44] **DeGennes, P.G.**, 1979. *Scaling Concepts in Polymer Physics*. Ithaca, NY: Cornell University Press.
- [45] **Mallam, S., Horkay, F., Hecht, A. M., Geissler, E.**, 1989. *Macromolecules*, **24**, 2896.
- [46] **Candou, S., Bastide, J., Delsantini M.**, 1982. *Adv. Polym. Sci.*, **44**, 27.
- [47] **Baumgarther, A., Picot, C.E.**, 1989. *Molecular Basis of Polymer Networks*, Springer, Berlin.
- [48] **Hecht, A.M., Duplessix, R., Geissler E.**, 1985. *Macromolecules*, **18**, 2167.
- [49] **Dusek, K., Prins, W.**, 1969. *Adv. Polym. Sci.* **6**,1.
- [50] **Schörder, U.P., Oppermann, W.**, 1997. *Macromol. Chem. Theory. Sim.*, **6**, 51.
- [51] **Okay, O.**, (1994). *Polymer* **35**:2613.
- [52] **Okay, O., Naghash, H.J., Capek, I.**, 1995. *Polymer* **36**:2413.
- [53] **Okay, O., Kurz, M., Lutz, K., Funke, W.**, 1995. *Macromolecules* **28**:2728.
- [54] **Debye, P.J., Bueche, A.M.**, 1949. *J. Appl. Phys.*, **20**,518.
- [55] **Stein, R.S.**, 1969. *Polymer Letters*, **7**,657.
- [56] **Stein, R.S., Soni, V.K., Yang, H., Erman, B.** (1988) "The Scattering of Light by Swollen Networks", in "Biological and Synthetic Networks", Ed. O. Kramer, Elsevier, NY, p. 383.
- [57] **Lovell, G.L., Bowman, C.N.**, 2003. *Polymer*, **44**, 39.

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