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Minimization of spatial inhomogeneity in polystyrene gels formed by free-radical mechanism

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Abstract

The spatial inhomogeneity in polystyrene (PS) gels has been investigated with the static light scattering technique. PS gels were prepared starting from styrene monomer and ethylene glycol dimethacrylate crosslinker in a homogeneous solution. The gel synthesis parameters varied were the crosslinker concentration, the primary chains length and the quality of the polymerization solvent. The gels were characterized by elasticity tests as well as by light scattering measurements at a gel state just after their preparation. The degree of spatial gel inhomogeneity decreased with decreasing crosslinker content, with decreasing primary chain length or, with increasing quality of the polymerization solvent. It was shown that the gel synthesis parameters varied mainly affect the distance between the pendant vinyl groups locating on the same macromolecule during the gel formation process. Increasing the distance between the pendant vinyl groups reduces the rate of the multiple crosslinking reactions so that the resulting PS gels exhibit a lesser degree of inhomogeneity.

Keywords: Polystyrene gels; Inhomogeneity; Static light scattering; Elastic modulus; Multiple crosslinking

1. Introduction

Polymeric gels are important materials of both fundamental and technological interest. Such materials are usually prepared by free-radical crosslinking copolymerization (FCC) of a monovinyl monomer (monomer) with a divinyl monomer (crosslinker) in a homogeneous solution. The formation mechanism of gels by FCC as well as their swelling properties and elastic behavior have been intensively studied in the last four decades. However, theories are still unable to predict their physical properties from the synthesis conditions. This is due to the several non-idealities of the gel formation system such as the different and conversion-dependent reactivities of the vinyl groups, cyclization, multiple crosslinking, and diffusion-controlled reactions [1,2].

FCC reactions involve at least three types of vinyl groups; those on monovinyl and divinyl monomers and those on polymer chains, i.e., pendant vinyl groups. During the course of the reactions, a pendant vinyl group is created when one of the vinyl groups on divinyl monomer reacts. The pendant vinyl group thus formed can then react by cyclization, crosslinking, and multiple crosslinking reactions, or can remain pendant [3–7]. As schematically illustrated in Fig. 1, cycles are formed when the macroradical attacks the pendant vinyl groups in the same kinetic chain; while multiple crosslinks are formed if the radical attacks double bonds pendant on other chains already chemically connected with the growing radical. Previous work shows that cyclization predominates in the early stages of the reaction [1]. In contrast to cyclization, multiple crosslinking is a second-order reaction, that is, a crosslinking reaction should precede each multiple crosslinkage (Fig. 1). The average

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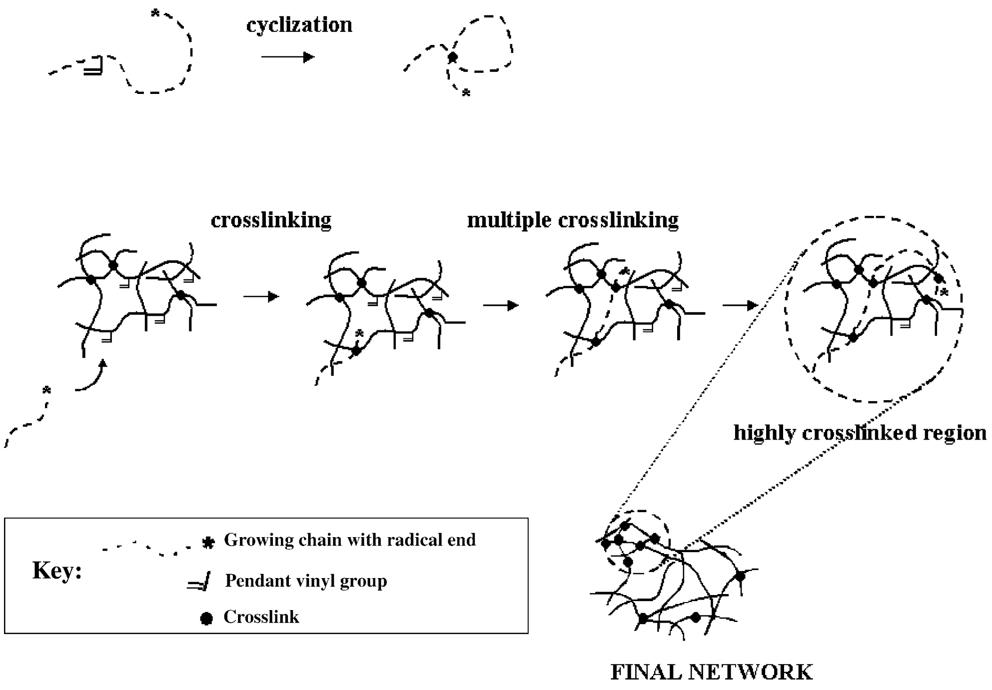

Fig. 1. Schematic representation of cyclization and multiple crosslinking reactions in free-radical crosslinking copolymerization. The area inside the dotted circle is a highly crosslinked region in the final network.

number of multiple crosslinks is zero at zero monomer conversion and it increases as the reaction proceeds because multiple crosslinking becomes the more probable the greater the molecules formed [3].

Polymer gels formed in such a non-ideal picture necessarily include defects affecting their physical properties such as swelling, elasticity, transparency, and permeability. One of the network defects, which have been extensively studied, is the gel inhomogeneity [8,9]. In contrast to the ideal gels with a homogeneous distribution of crosslinks throughout the gel sample, real gels always exhibit an inhomogeneous crosslink density distribution, known as the spatial gel inhomogeneity. Such inhomogeneity in the final materials is undesirable for applications because structural inhomogeneity results in a dramatic reduction in the strength of the crosslinked materials. Spatial inhomogeneity in gels formed by FCC originates from the inhomogeneous distribution of pendant double bonds in the gel formation system. As illustrated in Fig. 1, the reaction of a growing macroradical with a large number of pendant vinyl groups locating in a small region of space, that is, the crosslinking and the following multiple crosslinking reactions necessarily result in a local high concentration of crosslink points in the gel sample. The regions, where the multiple crosslinks form, will have a higher crosslink density then do others so that they will not swell as much as the other regions (Fig. 1). Thus, the inhomogeneous distribution of effective crosslinks and the resulting concentration fluctuations in the gels are a result of multiple crosslinking reactions.

The present study focuses on the problem of how to reduce the extent of spatial inhomogeneities in gels formed by FCC. The effects of the crosslinker content, the primary chain length and the solvating power of the polymerization solvent on the spatial inhomogeneity in polystyrene gels were investigated. For this purpose, three series of polystyrene gels were prepared starting from styrene (S) monomer and ethylene glycol dimethacrylate (EGDM) crosslinker in a homogeneous solution. In the first set, the crosslinker concentration was varied. In the second set, various amounts of a chain transfer agent, carbon tetrachloride, were added into the reaction system to vary the primary chain length. In the last set of experiments, mixtures of toluene (good solvent) and methanol (poor solvent) of various compositions were used as the polymerization solvent to vary the solvent quality of the gel formation system. The gels were characterized by elasticity tests as well as by static light scattering measurements at a gel state just after their preparation. The gel inhomogeneity was 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 was always larger than that from the polymer solution. The excess scattering over the scattering from polymer solution was related to the degree of the inhomogeneities in gels.

2. Experimental

2.1. Materials

The monomer styrene (S, Fluka) and the crosslinker ethylene glycol dimethacrylate (EGDM, Merck) were freed from the inhibitor by shaking with 10% aqueous NaOH, washing with water, and drying over Na_2SO_4. They were then distilled under reduced pressure. The initiator 2,2′ azobisisobutyronitrile (AIBN, Fluka) was recrystallized twice from methanol. HPLC—grade toluene, methanol, and carbon tetrachloride purchased from Riedel–de Haen were used for the synthesis of gels subjected to light scattering measurements. For the mechanical tests, the gels were prepared in reagent—grade solvents (Merck).

Gelation experiments were first carried out to find out the optimum gel formation condition suitable for the light scattering measurements. If the initial monomer concentration was above 40 vol.%, Rayleigh ratio versus the scattering vector q plots of the resulting polystyrene gels or polystyrene solutions exhibited marked curvature. In this high polymer concentration range, 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 strong q-dependence of the Rayleigh ratio [10]. Moreover, no gel formation was observed if the initial monomer concentration was less then 20 vol.%. Therefore, the initial monomer concentration was held constant between 20 and 40 vol.% throughout this work. No concentration effect on the scattered light intensity was observed in this range of the monomer concentration.

S–EGDM copolymerization reactions were carried out in toluene or in toluene/methanol mixtures at 60 ± 0.5 °C with AIBN as the initiator. The initiator concentration was held constant at 0.3 wt.% with respect to the monomers. The reaction time was one day. Mainly three sets of experiments were carried out. In the first set, the initial monomer concentration was kept constant at 30 vol.% while the amount of the crosslinker EGDM was varied between at 0 and 9.7 mol%. In the second set, polystyrene gels were prepared in the presence of various amounts of carbon tetrachloride as a chain transfer agent. The initial concentrations of the monomers and EGDM were 38 vol.% and 4.9 mol%, respectively. In the last set of experiments, toluene–methanol mixtures of various compositions were used as the polymerization solvent while the initial monomer and the EGDM concentrations were kept constant at 30 vol.% and 4.0 mol%, respectively. Details for the preparation of the polystyrene gels at 30 vol.% initial monomer concentration and at 3.1 mol% EGDM are given in the following scheme.

AIBN (0.0163 g) was dissolved in toluene and then, S (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 mixture was filtered directly into light scattering vials while for the mechanical tests, the mixture was transferred to glass tubes of 5 mm internal and 150 mm long. Both the tubes and the vials were placed in a thermostat at 60 °C and the polymerization was conducted 24 h.

2.2. Mechanical measurements

Uniaxial compression measurements were performed on gels just after their preparation. All the mechanical measurements were conducted in a thermostated room of 24 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus previously described [11]. Briefly, a cylindrical gel sample of about 5 mm in diameter and 7 mm in length was placed on a digital balance (Sartorius BP221S, readability and reproducibility: 0.1 mg). A load was transmitted vertically to the gel through a road fitted with a PTFE end-plate. The compressional force acting on the gel was calculated from the reading of the balance. The resulting deformation was measured after 20 s of relaxation by using a digital comparator (IDC type Digimatic Indicator 543–262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm. The measurements were conducted up to about 15% compression. Reversibility of the isotherms was tested by recording the force and the resulting deformation during both force—increasing and force—decreasing processes. The two processes yielded almost identical stress–strain relations. From the repeated measurements, the standard deviations in the modulus value were less than 3%. The sample weight loss during the measurements due to water evaporation was found to be negligible. The elastic modulus G_0 was determined from the slope of linear dependence

$$f = G_0(\alpha - \alpha^{-2}) \tag{1}$$

where f is the force acting per unit cross-sectional area of the undeformed gel specimen, and α is the deformation ratio (deformed length/initial length). In Fig. 2, the elastic moduli G_0 of gels are plotted against the gel synthesis parameters, namely the crosslinker (EGDM) concentration, the amount of the chain transfer agent CCl_4 and the solvent quality in terms of the volume fraction of methanol in the toluene–methanol mixture x_{MOH}.

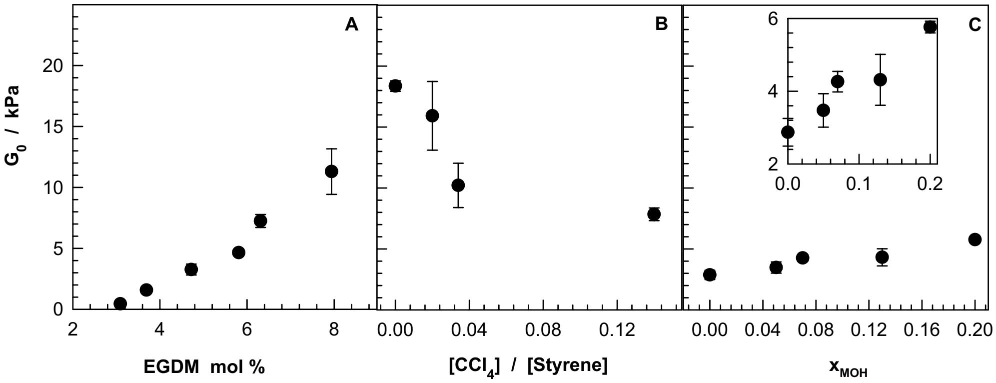

Fig. 2. The elastic modulus of gels after preparation G_0 shown as a function of the gel preparation parameters, i.e., the EGDM concentration (A), the chain transfer agent (CCl_4) concentration (B), and the solvent quality in terms of the volume fraction of methanol in toluene–methanol mixture x_{MOH} (C).

2.3. Light scattering experiments

For the light scattering measurements, the crosslinking polymerizations were carried out in the light scattering vials. All glassware was kept dust free by rinsing in hot acetone prior using. The solutions were filtered through membrane filters (pore size = 0.2 μm) directly into the vials. This process was carried out in a dust free glovebox. All the gels subjected to light scattering measurements were clear and appeared homogeneous to the eye. For the calculation 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 light scattering measurements were carried out at 24 °C using a commercial multi-angle light scattering DAWN EOS (Wyatt Technologies Corporation) equipped with a vertically polarized 30 mW gallium-arsenide laser operating at $\lambda = 690$ nm and 18 simultaneously detected scattering angles. The scattered light intensities were recorded from 30° to 142.5° which correspond to the scattering vector q range 7×10^{-4}–2.6×10^{-3} Å^{-1}, where $q = (4\pi n/\lambda)\sin(\theta/2)$, θ the scattering angle, λ the wavelength of the incident light in vacuum, n the refractive index of the medium. The light scattering system was calibrated against a toluene standard. To obtain the ensemble averaged light scattering intensity of gels, eight cycles of measurements with a small rotation of the vial between each cycle were averaged.

3. Results and discussion

3.1. Crosslinker concentration

Elasticity and light scattering measurements were carried out on polystyrene (PS) gels prepared at various crosslinker (EGDM) contents. The initial monomer concentration was fixed at 30 vol.%. As seen in Fig. 2A, increasing crosslinker content also increases the elastic moduli G_0 of gels. This is expected due to the simultaneous increase of the number of the crosslink points in the gel samples. Visual observations showed that 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. Therefore, only gel samples with less than 9 mol% EGDM were subjected to light scattering measurements. Fig. 3 shows

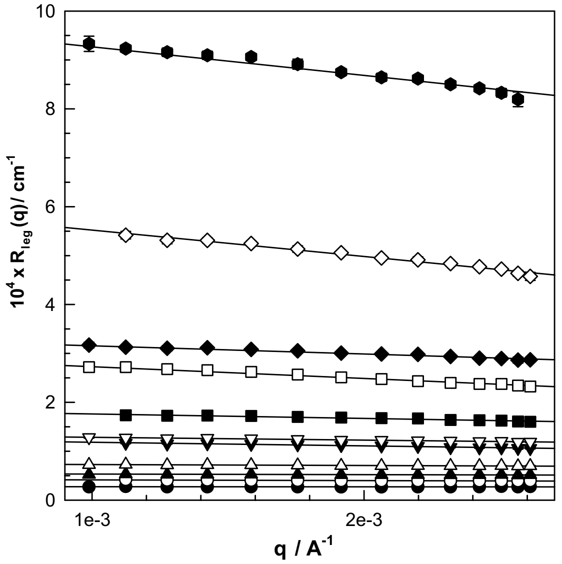

Fig. 3. Scattering light intensities from gels $R_{gel}(q)$ versus scattering vector q plots for PS gels of various crosslinker contents. Initial monomer concentration = 30 vol.%. EGDM mol% = 0 (●), 2.1 (○), 3.1 (▲), 3.7 (△), 4.2 (▼), 4.7 (▽), 5.2 (■), 5.8 (□), 6.3 (◆), 7.1 (◇), and 7.9 (⬢).

Rayleigh ratios from gel $R_{\mathrm{gel}}(q)$ versus the scattering vector q plots for PS gels of various EGDM contents. PS gels scatter much more light than the corresponding PS solution (0% EGDM sample) of the same concentration. Even the presence of a small amount of the crosslinker EGDM results in increased scattered light intensities from the gel samples. Furthermore, at low EGDM content, the scattered light intensity is nearly q-independent but for higher EGDM content, the q dependence becomes more pronounced. Excess scattering intensities from gels $R_{\mathrm{ex}}(q)$ were calculated as $R_{\mathrm{ex}}(q) = R_{\mathrm{gel}}(q) - R_{\mathrm{sol}}(q)$, where $R_{\mathrm{sol}}(q)$ is the Rayleigh ratio for polymer solution. To compare the excess scattering of different gels, we will focus on the scattering intensity measured at a fixed scattering vector $q = 1 \times 10^{-3}$ Å^{-1}. Fig. 4 shows the excess scattering at $q = 1 \times 10^{-3}$ Å^{-1} ($R_{\mathrm{ex},q}$) plotted as a function of EGDM%. The excess scattering from gels increases with increasing EGDM content. Since $R_{\mathrm{ex},q}$ is a measure of the spatial inhomogeneity in a gel, this indicates that the PS gel becomes more inhomogeneous with increasing EGDM concentration. This is due to the fact that the local pendant vinyl group concentration surrounding a growing macroradical is directly proportional to the crosslinker content in the feed. Thus, the higher the crosslinker content, the larger the number of multiple crosslinks will be and the greater the extent of gel inhomogeneity. Previous work shows similar results of the effect of crosslinker on the gel inhomogeneities [12–16]. Fig. 4 also shows that $R_{\mathrm{ex},q}$ increases first slightly up to about 4 mol% EGDM but then rapidly increases with a further increase in EGDM concentration, suggesting approaching partial phase separation. As shown in the inset to Fig. 4, a good linear behavior was obtained if the data points are redrawn in a semi-logarithmic plot, indicating an exponential law between $R_{\mathrm{ex},q}$ and EGDM%. This suggests the occurrence of a phase separation in the gel samples as the crosslinker content is increased.

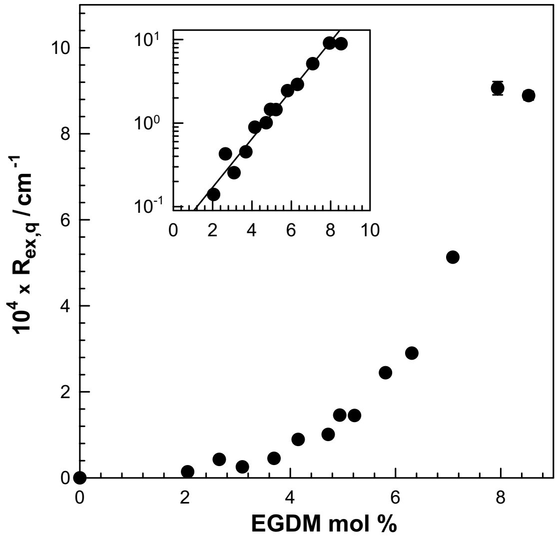

Fig. 4. The excess scattering $R_{\mathrm{ex},q}$ measured at $q = 1 \times 10^{-3}$ Å^{-1} shown as a function of EGDM mol%. The inset shows the same data in a semi-logarithmic plot.

3.2. Primary chain length

PS gels and the corresponding PS solutions were prepared in the presence of various amounts of carbon

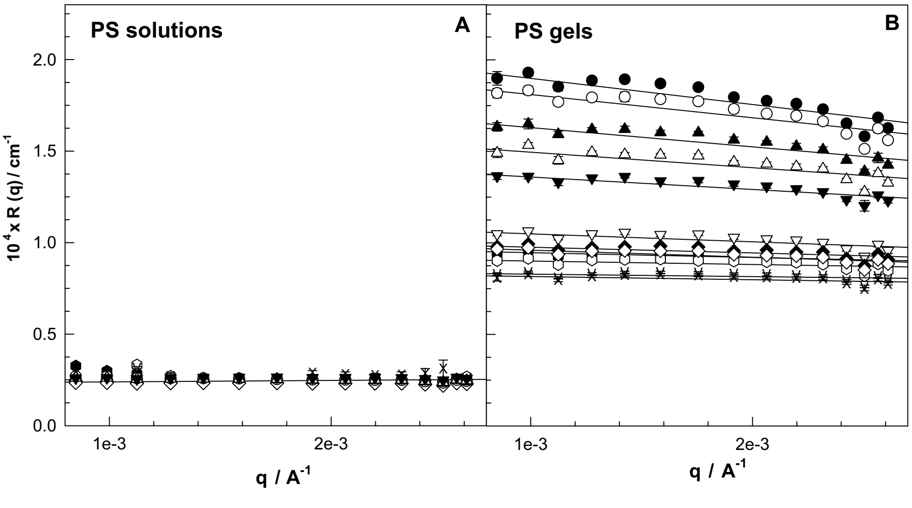

Fig. 5. Rayleigh ratio $R(q)$ versus scattering vector q plots for the PS gels (B) and for the corresponding linear PS solutions (A). Initial monomer concentration = 38 vol.%. EGDM = 4.9 mol%. CCl_4 concentration (mmol/mol styrene) = 0 (●), 3.4 (○), 8.5 (▲), 13.5 (△), 20.3 (▼), 34 (▽), 51 (◆), 68 (◇), 100 (⬡), 110 (⬢), 130 (×), and 160 (V).

tetrachloride CCl_4 as a chain transfer agent. The total monomer and the EGDM concentrations were set to 38 vol.% and 4.9 mol%, respectively. In this way, changing the chain transfer agent concentration controlled the size of the growing macroradicals [17]. As seen in Fig. 2B, the elastic modulus of gels decreases with increasing amount of CCl_4 present in the gel formation system. This is due to the formation of shorter primary molecules as the amount of CCl_4 is increased. Thus, as the primary chains become shorter, the number of terminal chains, which make no contribution to the network elasticity, increases. As a consequence, the elastic modulus decreases on rising CCl_4 concentration. Fig. 5 shows Rayleigh ratios $R(q)$ versus the scattering vector q plots for PS gels and for the corresponding PS solutions. For polymer solutions, the light scattering intensity does not change much with the CCl_4 concentration; All the $R_{\mathrm{sol}}(q)$ versus q plots for polymer solutions cross each other. However, the scattering light intensity from gels $R_{\mathrm{gel}}(q)$ decreases continuously with increasing CCl_4 concentration. In Fig. 6, the scattering intensities from gels $R_{\mathrm{gel},q}$ (filled circles), from solutions $R_{\mathrm{sol},q}$ (open symbols) and the excess scattering $R_{\mathrm{ex},q}$ (filled triangles), all measured at $q = 1 \times 10^{-3}$ Å^{-1}, are plotted against the CCl_4 concentration. In polymer solutions, the scattered light intensity $R_{\mathrm{sol},q}$ increases only slightly with increasing concentration of CCl_4. However, $R_{\mathrm{gel},q}$ and $R_{\mathrm{ex},q}$ decrease first rapidly up to 0.03 mol CCl_4/mol styrene but then slightly as the amount of CCl_4 is increased. At high CCl_4 concentrations, the scattered light intensity from gel approaches to that from the corresponding polymer solution. These results clearly demonstrate that the extent of the inhomogeneity in PS gels is strongly reduced by the addition of a chain transfer agent in the gel formation system. This phenomenon can be explained with decreasing primary chain length on rising CCl_4 concentrations, which reduces the extent of the multiple crosslinking reactions and thus leads to a more homogeneous distribution of the crosslink points along the gel sample.

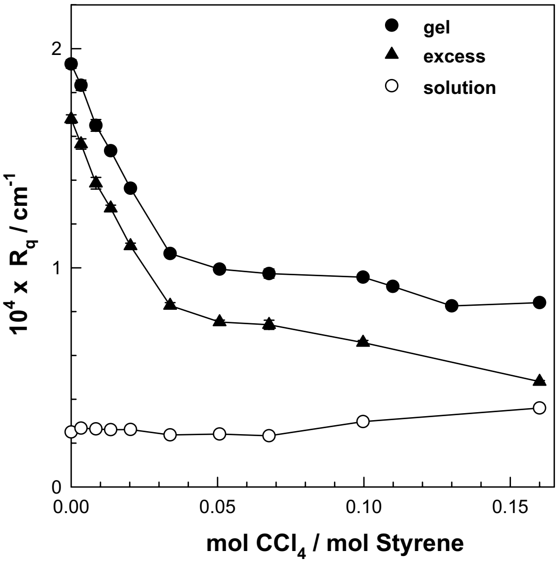

Fig. 6. Scattering light intensities from gels $R_{\mathrm{gel},q}$ (filled circles), from PS solutions $R_{\mathrm{sol},q}$ (open circles) and the excess scattering $R_{\mathrm{ex},q}$ (filled triangles) measured at $q = 1 \times 10^{-3}$ Å^{-1} shown as a function of CCl_4 concentration.

3.3. Solvent quality

The solvating power of the solvent used in the gel formation process is also expected to affect the degree of the spatial inhomogeneity of gels. A series of PS gels and PS solutions were prepared in mixtures of toluene and methanol, which are good and poor solvent for PS, respectively. The volume fraction of methanol in the solvent mixture x_{MOH} was varied between 0 and 0.2. All the gels and solutions prepared in this range of methanol concentration were homogeneous in appearance and optically clear. They were subjected to light scattering measurements. The elastic moduli of gels G_0 are shown in Fig. 2C plotted against the methanol volume fraction x_{MOH}. Although the effect of the solvent quality on the elastic modulus is only slight, the trend seen in the figure is that G_0 increases with increasing x_{MOH}, i.e., with decreasing solvating power of the polymerization solvent. This is probably due to the increasing proximity of pendant vinyl groups as the solvent quality becomes poorer, which increases the probability of both crosslinking and multiple crosslinking reactions. In Fig. 7, the scattered light intensities from gels $R_{\mathrm{gel},q}$, from solutions, $R_{\mathrm{sol},q}$ and the excess scattering $R_{\mathrm{ex},q}$ at $q = 1 \times 10^{-3}$ A^{-1} are shown as a function of the methanol concentration x_{MOH}. It is seen that both $R_{\mathrm{gel},q}$ and $R_{\mathrm{sol},q}$ increase as the polymer–solvent interaction becomes poorer. Compared to $R_{\mathrm{sol},q}$, $R_{\mathrm{gel},q}$ increases more rapid with methanol content so that the excess scattering increases with methanol concentration. This increase is first slight up to $x_{\mathrm{MOH}} = 0.17$ but then rapid at higher methanol concentrations. Thus, the results show that decreasing solvent quality increases the spatial inhomogeneity in PS gels. Previous research also shows the importance of solvent quality on crosslinking and polymer network formation [18]. If the polymer–solvent interaction is good during crosslinking, a pendant vinyl group will be found more difficult by radicals due to the thermodynamic excluded volume effect. Thus, the presence of larger coils in the polymerization system will reduce the crosslinking and multiple crosslinking reactions. In another case, if the solvent–polymer interactions are poor, the chains will coil more rather then stretch out, and the probability of crosslinking and multiple crosslinking is greater due to increased proximity of the pendant

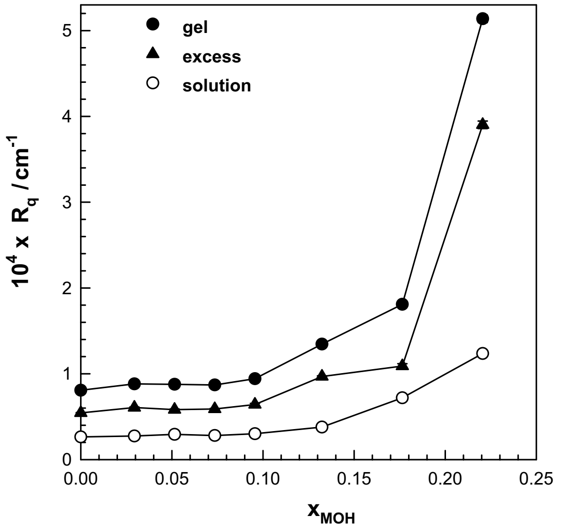

Fig. 7. Scattering light intensities from gels $R_{gel,q}$ (filled circles), from PS solutions $R_{sol,q}$ (open circles) and the excess scattering $R_{ex,q}$ (filled triangles) measured at $q = 1 \times 10^{-3}$ Å^{-1} shown as a function of the methanol concentration x_{MOH}. Initial monomer concentration = 30 vol.%. EGDM = 4.0 mol%.

double bonds [19]. As a result, a decrease in the solvent quality during the gel formation increases both the elastic moduli and the spatial inhomogeneity of gels.

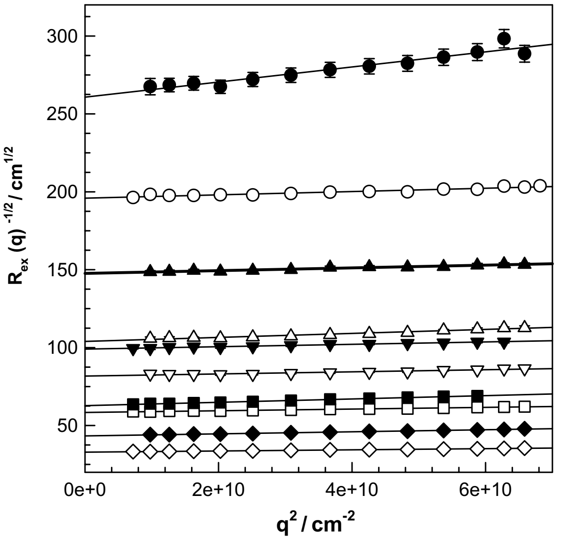

Fig. 8. Debye–Bueche plots for PS gels prepared at various EGDM mol %. EGDM mol% = 2.1 (●), 3.1 (○), 3.7 (▲), 4.2 (△), 4.7 (▼), 5.2 (▽), 5.8 (■), 6.3 (□), 7.1 (◆), and 7.9 (◇).

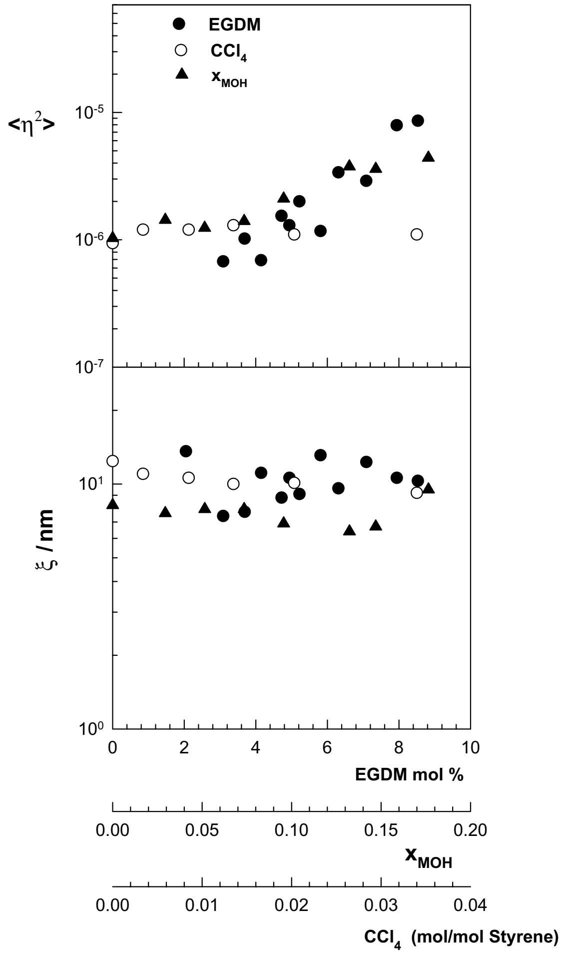

Fig. 9. The mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ and the correlation length of the scatterers ξ in PS gels shown as a function of the gel synthesis parameters.

3.4. Debye–Bueche analysis of the light scattering data

To interpret light scattering results from gels, several functional forms of excess scattering $R_{ex}(q)$ have been proposed empirically, i.e., Debye–Bueche [20–23], Guinier [24–27], and Ornstein–Zernicke functions [24–28]. For example, the excess scattering was given by the Debye–Bueche function as

$$R_{ex}(q) = \frac{4\pi K \xi^3 \langle \eta^2 \rangle}{(1 + q^2 \xi^2)^2} \tag{2}$$

where K being the optical constant, $K = 8\pi^2 n^2 \lambda^{-4}$, ξ is the correlation length of the scatterers, and $\langle \eta^2 \rangle$ is the mean square fluctuation of the refractive index. According to Eq. (2), the slope and the intercept of $R_{ex}(q)^{-1/2}$ versus q^2 plot (Debye–Bueche plot) give ξ and $\langle \eta^2 \rangle$ of a gel sample. In Fig. 8, some of the data points obtained from PS gels of various EGDM contents are replotted in the form of Debye–Bueche plots. It is seen that straight lines are obtained in this analysis, indicating that the Debye–Bueche function works well. Similar linear plots were also obtained for other sets of PS gels or, by fitting the experimental data to the Guinier and Ornstein–Zernicke functions. The values of ξ and $\langle\eta^2\rangle$ calculated from the Debye–Bueche analysis are shown in Fig. 9 plotted against the gel synthesis parameters, namely EGDM mol%, the chain transfer agent (CCl_4) concentration, and the methanol volume fraction in the solvent mixture x_{MOH}. The correlation length of the scatterers ξ, i.e., the extension of the inhomogeneities in PS gels was found to be 10 ± 3 nm and, almost independent of the gel synthesis parameters. The extent of the concentration fluctuations $\langle\eta^2\rangle$ is in the range 10^{-7}–10^{-5} and it increases with increasing crosslinker (EGDM) concentration or with increasing x_{MOH}, i.e., with decreasing quality of the polymerization solvent. The results also show that, in contrast to the excess scattering data shown in Fig. 6, $\langle\eta^2\rangle$ does not change much with the chain transfer agent concentration, probably due to the simultaneous variation of the chain length of the primary molecules.

3.5. Conditions of approaching homogeneous PS gels

Synthesis of a homogeneous gel by FCC requires a homogeneous distribution of the pendant vinyl groups along the gel formation system. However, experimental verification of this condition is difficult to achieve due to the fact that the divinyl monomer reactivity is at least twice the reactivity of monovinyl monomer [1,2]. As a result, the molecules formed earlier have a higher concentration of pendant vinyl group than those formed in later stages of the crosslinking polymerization so that an inhomogeneous pendant unsaturation distribution necessarily results. Here, we have shown methods for obtaining gels by free-radical mechanism with a minimum degree of spatial inhomogeneity. The experimental results show that the degree of spatial inhomogeneity in polystyrene gels decreases with decreasing crosslinker content, with increasing amount of a chain transfer agent or, with increasing quality of the polymerization solvent. As schematically illustrated in Fig. 10, the gel synthesis parameters varied mainly affect the distance between the pendant vinyl groups locating on the same macromolecule during the gel formation process. For example, a decrease in the crosslinker concentration or in the molecular weight of the primary molecules will necessarily decrease the local concentration of pendant vinyl groups (A and B). As the polymer–solvent interaction becomes better; the polymer molecules will expand more, so that the distance between the adjacent pendant vinyl groups will increase (C). Increasing the distance between the pendant vinyl groups reduces the rate of the multiple crosslinking reactions so that the resulting gels become more homogeneous. The results thus suggest that the factors decreasing the proximity of

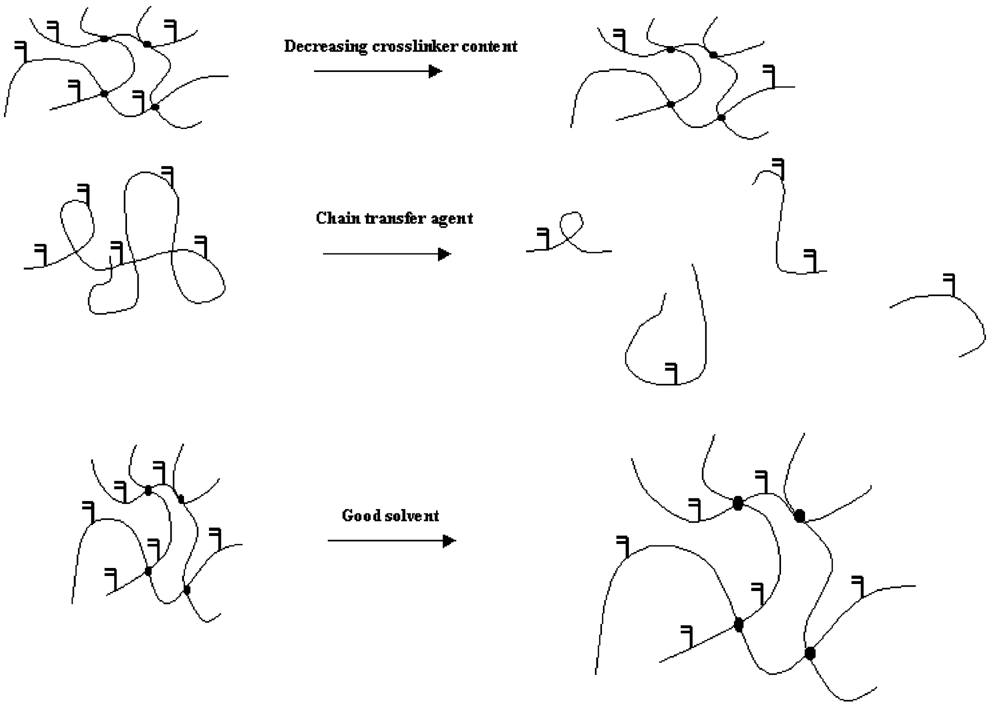

Fig. 10. Schematic representation of the effects of the gel synthesis parameters on the proximity of pendant vinyl groups during the gel formation process.

pendant vinyl groups lead to the minimization of spatial gel inhomogeneities.

Acknowledgements

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