

# Study of Ethylene–Propylene Copolymer Thermoreversible Gels

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**ABSTRACT:** Molecular structure and rheological properties of ethylene–propylene (EP) random copolymer gels formed in toluene and methylcyclohexane, respectively, have been investigated by small-angle neutron scattering (SANS) and oscillatory shear. In both solvents, SANS results are analyzed by considering a fiberlike structure with a radius cross-section distribution function expressed by  $w(r) \sim r^{-2}$ . It is shown that a small change in the EP copolymer ethylene content has a large effect on the density of network connecting fibers but a much smaller effect on the diameter of the fibers. Oscillatory shear experiments reveal that the relaxation rate of the elastic modulus increases with decreasing EP copolymer ethylene content. This behavior indicates a decrease in the density of connections between fibers with decreasing ethylene content. The relationship between the elastic modulus and polymer concentration has also been examined. The results suggest, in light of the theory developed by Jones and Marques for rigid networks, that the rigidity of fibers formed in the gel is achieved only locally.

## Introduction

The propensity of ethylene–propylene (EP) random copolymers to form thermoreversible gels has been investigated in a variety of organic solvents.<sup>1</sup> A number of studies have been published on EP copolymer gels.<sup>1–4</sup> These studies mainly focused on the influence of polymer concentration, molecular mass, ethylene content, and solvent type on the gel-melting temperature. The data obtained from these studies were also used to determine the average size of the crystalline junctions or crystallites formed by crystallizable ethylene sequences along EP copolymer chains. The average size of the crystallites forming the cross-links along the polymer chains was calculated from gel-melting temperatures using the Takahashi theory.<sup>5</sup> It was found that the crystallite size decreases with increasing propylene content and decreases with decreasing number-average ethylene sequence length. Furthermore, it was shown that crystalline junctions are formed by ethylene sequences longer than or equal to five units. However, the reliability of this prediction is still a question since the accuracy of the Takahashi theory to predict the size of the crystalline junctions in the gel remains to be proven. Indeed, the Takahashi theory is derived from the melting temperature depression of crystallites in a solvent as defined by Flory<sup>6</sup> and Mandelkern,<sup>7</sup> assuming that the physical gel junctions are small enough to be regarded as fringed-micelle type crystallites, which are considered pointlike. However, in many polymer gels the physical junctions are not pointlike junctions but are made of crystallites. In particular, in the case of the ethylene–propylene copolymer, the gel formation and gel melting are known to proceed via a first-order transition,<sup>2</sup> suggesting that the physical junctions are composed of crystallites that are not pointlike. Thus, the application of the Takahashi theory to EP copolymer gel appears to be inadequate.

**Table 1. Molecular Mass and Ethylene Contents of EP Copolymers Used for Our Study**

polymer	ethylene content (mol fraction %)	molecular mass	polydispersity
EP 1	73.6 ± 1.0	307 000 ± 30 700	2.44 ± 0.35
EP 2	77.3 ± 1.0	283 000 ± 28 300	2.36 ± 0.33

Even though a considerable amount of work has been done in this area, the lack of a reliable EP copolymer gel structural data prevents a complete understanding of the EP copolymer gelation mechanism. The purpose of this paper is to overcome some of these problems by characterizing the gel structure directly from small-angle neutron scattering (SANS). The gel structure was studied in toluene and methylcyclohexane with two different ethylene contents containing a mole fraction of approximately ( $x_E = 73\%$  and  $x_E = 77\%$ ) ethylene. We found that EP copolymer gels display a fiberlike structure. In particular, we found that the ethylene content has a large effect on the density of network connecting fibers, but a much smaller effect on the diameter of the fibers. We also report preliminary results on the viscoelastic properties of EP copolymer gels. The influence of ethylene content, solvent type, and temperature on the viscoelastic properties of EP copolymer gels is then compared with the structural data obtained by neutron scattering.

## Experimental Section

**(1) Materials.** Two EP copolymers were used in this study. EP copolymer samples were prepared by conventional Ziegler–Natta polymerization. The ethylene content was determined by FTIR; the molecular mass and polydispersity were obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C. All temperatures given have a range of ±1 °C, which is standard for the temperature controllers used. Physical properties are listed in Table 1. Both protonated and deuterated (mole fraction > 99% deuterium) toluene and methylcyclohexane were purchased from Aldrich and used without further purification.<sup>8</sup>

The GPC measurements give polyethylene equivalent molecular masses which have been shown to have a relative

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standard uncertainty of  $\pm 10\%$  through previous work leading to a standard uncertainty in polydispersity of  $\pm 0.3$ . The ethylene content is always reported in terms of mole fraction, which is similarly estimated to have a standard uncertainty of  $\pm 1.0\%$ . All concentrations are reported as volume fractions.

**(2) Sample Preparation.** All EP copolymer solutions were prepared in hermetically sealed test tubes by heating the mixtures above the boiling point of either toluene or methylcyclohexane until complete dissolution of the polymer and the appearance of a transparent and homogeneous solution had occurred.

**(3) Scanning Electron Microscopy (SEM).** A drop of solution was deposited onto the sample holder, put into a beaker with a sealed cover, and chilled in a methanol bath kept at  $-30\text{ }^\circ\text{C}$  for 1 h to make the gel. The gel film was then dried and finally shadowed and coated according to standard SEM sample preparation procedure. SEM micrographs were taken with a JEOL 5800LV scanning electron microscope.

**(4) Small-Angle Neutron Scattering.** Experiments were carried out with the 8-m SANS at NIST. The  $q$  range accessible was typically  $0.1\text{ nm}^{-1} < q < 1.7\text{ nm}^{-1}$ . Sample solutions were prepared in test tubes and poured into quartz cells of 1 mm thickness. The structures of gels formed from polymer solutions containing volume fractions (3% and 6%) of EP copolymers were investigated in deuterated toluene and deuterated methylcyclohexane, at both  $-20$  and  $-35\text{ }^\circ\text{C}$ . To ensure gel formation, the solutions were aged for 30 min prior to any measurement. Measured scattering intensities were first normalized to remove dependency on sample thickness, transmission, and the empty-cell and "beam-blocked" background. Then absolute intensity was obtained by correction made with respect to the scattering of water taken as the standard. Finally, to extract the coherent scattering due to polymer chains, the absolute intensity was further corrected by subtracting the incoherent scattering generated by the deuterated solvent and that of the polymer chains. The latter was calculated through a method devised by Fazel et al.<sup>9</sup>

Plots of small-angle scattering data have been calculated from circular averaging of two-dimensional files. The uncertainties are calculated as the estimated standard deviation of the mean, and the total combined uncertainty is not given as comparisons are made with data obtained under the same conditions. In cases where the limits are smaller than the plotted symbols, the limits are left out for clarity. In data plots with uncertainties larger than the symbols, representative confidence limits are plotted at appropriate places. Fits of the scattering data are made by a least-squares fit of the data giving an average and a standard deviation to the fit; this is true for fit values such as radius of cross-section and exponents.

The absolute intensity scattered by the polymer is given by

$$I_A(q) = KC_{\text{pol}}S_p(q) \quad (1)$$

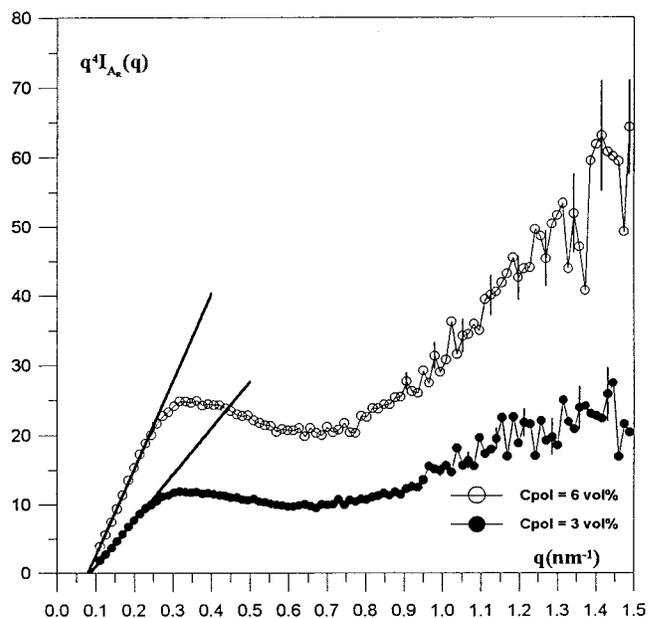
where  $C_{\text{pol}}$  and  $S_p(q)$  are the polymer concentration and the scattering function of the polymer chains, respectively. Also,  $q$  is the scattering vector, and  $K$  is a constant given by

$$K = \frac{N_A(a_p - Y a_s)^2}{m^2} \quad (2)$$

where  $N_A$  is the Avogadro's number,  $m$  is the monomer molecular mass,  $a_p$  and  $a_s$  are the scattering lengths of the polymer species and the solvent, respectively, and  $Y = v_p/v_s$  is the ratio of the molar volumes of the polymer and solvent. The reduced form of the absolute scattering intensity then becomes

$$I_{A_r}(q) = I_A/K = C_{\text{pol}}S_p(q) \quad (3)$$

**(5) Viscoelasticity Measurements.** Viscoelasticity measurements were performed on a Paar Physica UDS200 rheometer using a parallel plate geometry (50 mm diameter plate). All data were collected from the linear elastic region. Liquid



**Figure 1.** Intensity scattered by EP copolymer ( $x_E =$  mole fraction 77.3%) gels prepared from volume fraction (6% and 3%) toluene solutions, respectively. ( $q^4 I(q)$  vs  $q$  representation).

nitrogen was used as the coolant. Solutions were poured onto the bottom plate and aged at the desired temperature to ensure gel formation. To avoid both solvent evaporation and condensation of water, the sample was covered throughout the entire period of the experiment.

## Results and Discussion

**(A) Structure of EP copolymer gels. (1) EP Copolymer Gels in Toluene.** Figure 1 shows plots of  $q^4 I(q)$  vs  $q$  of scattering data measured from gels formed in volume fraction 3% and 6% toluene solutions, which were prepared from a mole fraction 77.3% ethylene EP copolymer. Each plot can be segmented into three regions. In region 1, which is also called the linear region or transitional region, the plot increases linearly; in region 2, the plot becomes nonlinear and reaches a maximum, and in region 3 the intensity increases as  $q^2$ . Both curves can be analyzed in the low  $q$  range via a theoretical model proposed by Guenet et al.<sup>10</sup> for any system consisting of a cross section of polydispersed fibers.

For a population of fibers with a radius cross-section distribution function expressed by  $w(r) \sim r^{-1}$  with two cutoff radii  $r_{\text{min}}$  and  $r_{\text{max}}$ , the intensity in region 1 can be written as follows:

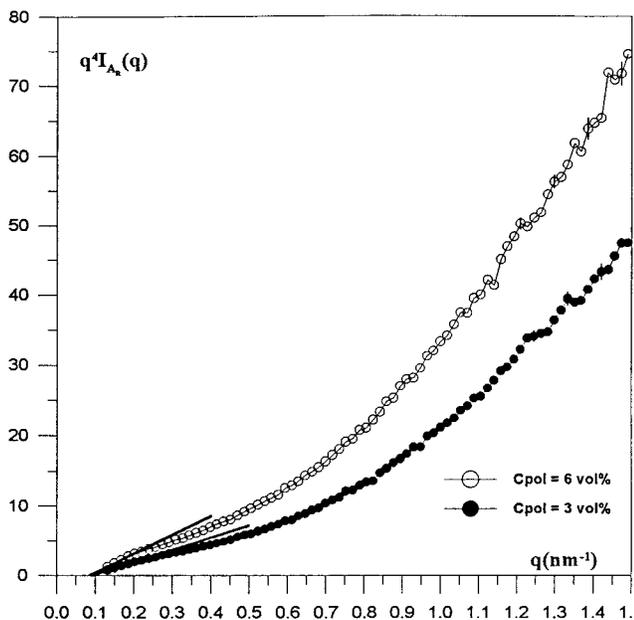
$$\frac{q^4 I_{A_r}(q)}{C_{\text{pol}}} = 2\pi^2 \rho \left[ q - \frac{2}{\pi r_{\text{max}}} \right] \times \ln^{-1} \left( \frac{r_{\text{max}}}{r_{\text{min}}} \right) \quad (4)$$

Here  $\rho$  is the polymer density of the fibers. The value of  $r_{\text{max}}$  can be determined from the intercept on the  $q$  axis,  $q_0$ :

$$r_{\text{max}} = \frac{2}{\pi q_0} \quad (5)$$

In region 2, which is the so-called Porod range or plateau regime, the intensity is given by

$$q^4 I_{A_r}(q) = \frac{4\pi\rho C_{\text{pol}}}{r_n} + \frac{A}{q^2} \quad (6)$$



**Figure 2.** Intensity scattered by EP copolymer ( $x_E$  = mole fraction 73.6%) gels prepared from volume fraction (6% and 3%) toluene solutions, respectively.

where  $r_n$  is the number-average mean cross section radius and can be expressed as a function of  $r_{\max}$  and  $r_{\min}$  by

$$\frac{1}{r_n} = \left[ \frac{1}{r_{\min}} - \frac{1}{r_{\max}} \right] \times \ln^{-1} \left( \frac{r_{\max}}{r_{\min}} \right) \quad (7)$$

The constant  $A$  is related to the number of connections between fibers per unit volume.<sup>10,11</sup> As  $q$  increases beyond region 1, the  $q^{-2}$  term becomes negligible and a plateau regime is reached. The value corresponding to the maximum just before the Porod regime is assumed to be proportional to the number of junctions.

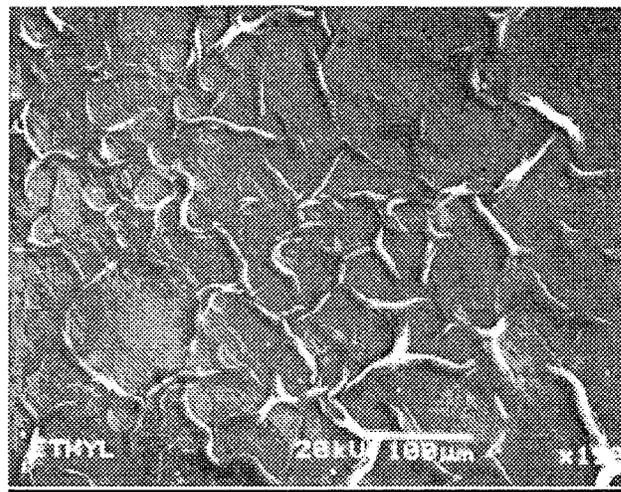
From the scattering vector  $q^*$ , which is the  $q$  value at which region 2 (or the plateau regime) intersects with the straight line drawn from region 1 (the linear region), the value of  $r_{\min}$  can be determined through

$$r_{\min} = \frac{2}{\pi q^*} \quad (8)$$

For the volume fraction 6% polymer solution, the values of  $r_{\max}$  and  $r_{\min}$  were found to be  $8 \pm 0.3$  nm and  $2.6 \pm 0.15$  nm, respectively, whereas for the volume fraction 3% polymer solution, the values obtained for  $r_{\max}$  and  $r_{\min}$  are  $7.5 \pm 0.3$  nm and  $2.75 \pm 0.2$  nm, respectively. Values of  $r_{\max}$  and  $r_{\min}$  remain constant at these two concentrations. The uncertainties of the fits are a standard deviation calculated from the goodness of a linear fit.

As  $q$  further increases, we observe a departure from the plateau regime, and the scattering intensity varies as  $q^{-2}$ . This departure can be due to the presence of either the free chain population (disconnected from the network) and/or pendant chains (attached by one end to the network). However, the existence of the plateau regime indicates that the fraction of loose chain is rather low.<sup>12</sup> This will be further addressed later in the viscoelasticity section.

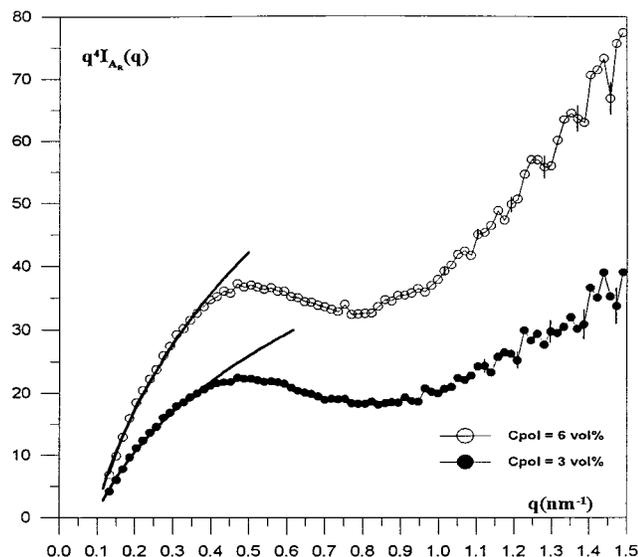
Figure 2 shows the results obtained with gels formed in the toluene solution of copolymer mole fraction 73.5%



**Figure 3.** SEM picture of a dried EP copolymer ( $x_E$  = mole fraction 73.6%) gel prepared in toluene at volume fraction 3%.

EP solution in toluene, at volume fraction copolymer 6% and 3%. The overall shape of the curves shows that the ethylene content has a dramatic effect on the structure of the gels formed at  $-20$  °C. Unlike the experiments carried out with  $x_E = 77.3\%$  ethylene content, we do not observe any maximum from either plot. The absence of a maximum indicates a smaller number of connections between fibers. In the low  $q$  range, where the plot corresponds to region 1, with gels prepared from mole fraction 77.3% EP copolymer, it is difficult to conclude if the distribution of radii can be described by  $w(r) \sim r^{-1}$  or by  $w(r) \sim r^{-\lambda}$ . It appears that linearity holds only in a small range. If the  $w(r) \sim r^{-1}$  cross-sectional distribution function is assumed, a  $r_{\max}$  value of  $7.0 \pm 0.4$  nm for the gel prepared from mole fraction 3% deuterated toluene solution and a corresponding  $r_{\max}$  value of  $7.4 \pm 0.25$  nm for the mole fraction 6% deuterated toluene solution would be found. Because of the absence of a region 2 (Porod plateau), the determination of  $r_{\min}$  was impossible. The diameter of the fibers formed in the gel decreases slightly with decreasing ethylene content. A smaller diameter of fibers and a smaller number of connections between fibers for the gels formed by the mole fraction 73.6% ethylene EP copolymer are consistent with the expectation that lowering the ethylene content can decrease the EP copolymer gelation tendency.

It is noteworthy that the interpretation of the SANS data as a fiber structure is justifiable by the SEM observation. As is shown in Figure 3, a fiberlike structure was obtained with the dried gel prepared from a toluene solution. A similar observation had been made from a dried gel film prepared from a carbon disulfide solution.<sup>2</sup> Though the diameters of the fibers shown in this picture are generally much larger than those measured by SANS, the results of the two methods are consistent. Two factors are expected to affect the diameters here: the polymer concentration and the procedure used for the SEM sample preparation. It is reasonable to expect that coalescence of the fibers can occur during the sample drying process. From practical experience, the turbidity level of the solution prepared for the SEM experiment could provide a good indication whether the actual fibril size is closer to the value found by SEM or the one measured by SANS. At  $-20$  °C, the solution displays a slight turbidity. This result means



**Figure 4.** Intensity scattered by EP copolymer ( $x_E =$  mole fraction 77.3%) gels prepared from volume fraction 6% and 3% methylcyclohexane solutions, respectively.

that the size measured by SANS is most probably correct.

## (2) EP Copolymer Gels in Methylcyclohexane.

The plots of the scattering data obtained with gels formed in two methylcyclohexane solutions (volume fraction 3% and 6%) prepared from the mole fraction 77.3% EP copolymer are shown in Figure 4. Unlike the gels formed in toluene, the scattering intensity plots do not display a linear variation in the transitional region (region 1). The data can be interpreted by considering a distribution of the fibers with a cross-section distribution function of  $w(r) \sim r^{-\lambda}$  and the scattering intensity can then be written as

$$\frac{q^4 I_{AR}(q)}{C_{pol}} = 4\pi^2 \rho \left[ A(\lambda) q^\lambda - \frac{1}{\lambda \pi r_{max}^\lambda} \right] / \int_{r_{min}}^{r_{max}} w(r) dr \quad (9a)$$

where  $A(\lambda)$  is a constant expressed as

$$A(\lambda) = \frac{\Gamma(\lambda) \Gamma\left(\frac{3-\lambda}{2}\right)}{2^\lambda \Gamma\left(\frac{\lambda+1}{2}\right) \Gamma\left(\frac{\lambda+3}{2}\right) \Gamma\left(\frac{\lambda+1}{2}\right)} \quad (9b)$$

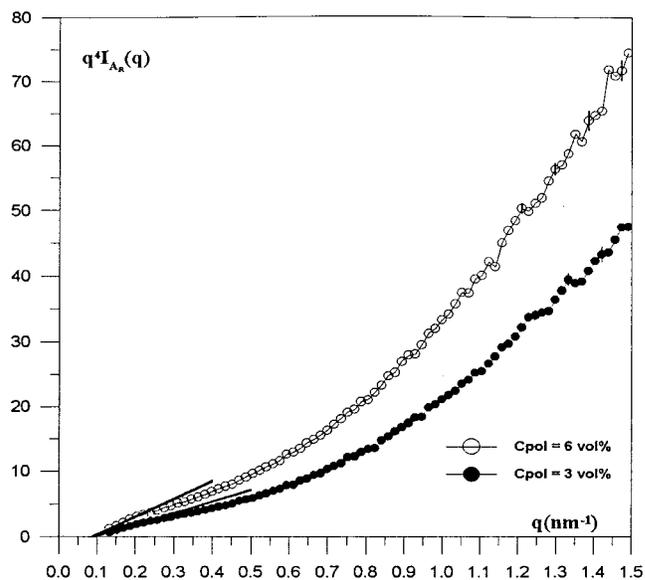
where  $\Gamma$  is the gamma function. We found that  $\lambda$  is equal to  $0.23 \pm 0.05$  for the gels formed at these two polymer concentrations. The value of  $r_{max}$  is related to the intercept  $q_0$  with the  $q$  axis through the following equation:

$$r_{max} = \frac{1}{q_0 [\lambda \pi A(\lambda)]^{1/\lambda}} \quad (10)$$

Similarly,  $r_{min}$  can be obtained from  $q^*$  through

$$r_{min} = \frac{1}{q^* [\lambda \pi A(\lambda)]^{1/\lambda}} \quad (11)$$

For the volume fraction 6% polymer solution, we found that  $r_{max} = 6.4 \pm 0.3$  nm and  $r_{min} = 1.65 \pm 0.20$  nm. Likewise, for the volume fraction 3% polymer solution, we found that  $r_{max}$  and  $r_{min}$  are  $6.5 \pm 0.2$  nm and  $1.8 \pm 0.2$  nm, respectively. Thus,  $r_{max}$  and  $r_{min}$  appear to be



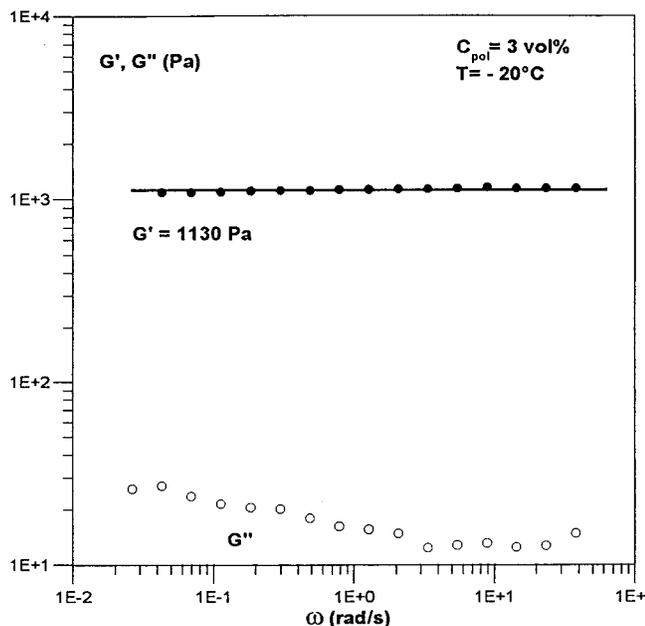
**Figure 5.** Intensity scattered by EP copolymer ( $x_E =$  mole fraction 73.6%) gels prepared from volume fraction 6% and 3% methylcyclohexane solutions, respectively.

independent of the polymer concentration within the range of concentrations studied.

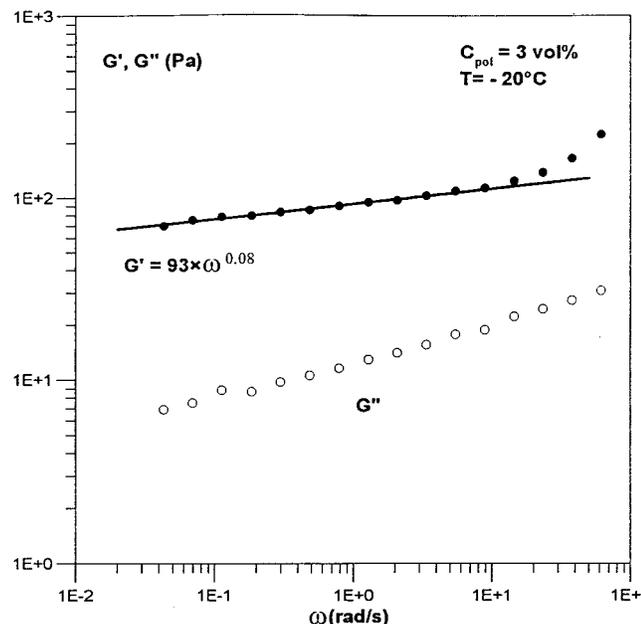
Figure 5 shows the corresponding plots from the scattering data obtained at  $-35$  °C for gels prepared in deuterated methylcyclohexane solutions with the low ethylene content EP copolymer ( $x_E =$  mole fraction 73.6%). As in toluene, the absence of a maximum indicates that the number of connections between the fibers decreases as a result of lowering the ethylene content. Using the same analysis for the low  $q$  range as for region 1 of the gels prepared from the  $x_E = 77.3\%$  ethylene, we found that a  $\lambda$  value of  $1.38 \pm 0.10$  for the gel prepared at volume fraction 3% solution and a  $\lambda$  value of  $1.25 \pm 0.15$  for the gel prepared at volume fraction 6% solution. The values of  $r_{max}$  were found to be  $4.85 \pm 0.50$  nm for the low concentration gel and  $5.9 \pm 0.4$  nm for the high concentration gel, respectively. The results are consistent with the trend observed in toluene. It appears that ethylene content does not have a big effect on the fiber radius.

## (B) Viscoelastic Properties of EP Copolymer Gels.

The dynamic moduli  $G'$  and  $G''$  measured at  $-20$  °C for the gel prepared from a volume fraction 3% EP copolymer ( $x_E =$  mole fraction 77.5%) toluene solution are shown in Figure 6. Throughout the entire range of frequencies investigated,  $G'$  is virtually constant while  $G''$  is much smaller than  $G'$ . These results indicate that the gel does not display any relaxation process. This behavior agrees with the mechanical definition of a gel. A polymer gel should display a solidlike behavior and therefore it should display an elastic modulus at zero frequency. However, such behavior is not always observed in thermoreversible gels. In many cases, the gel deforms almost permanently under mechanical stress and exhibits a relaxation behavior.<sup>13-15</sup> This behavior can be attributed to the weakness of the junctions between polymer chains. Such weak junctions are readily broken under a low stress. The effect of the ethylene content on the dynamic moduli is shown in Figure 7. Unlike the gel formed by the mole fraction 77.3% EP copolymer, we find that the gel prepared from mole fraction 73.6% EP copolymer displays a relaxation behavior because at low frequencies  $G'$  varies as  $\omega^m$ ,

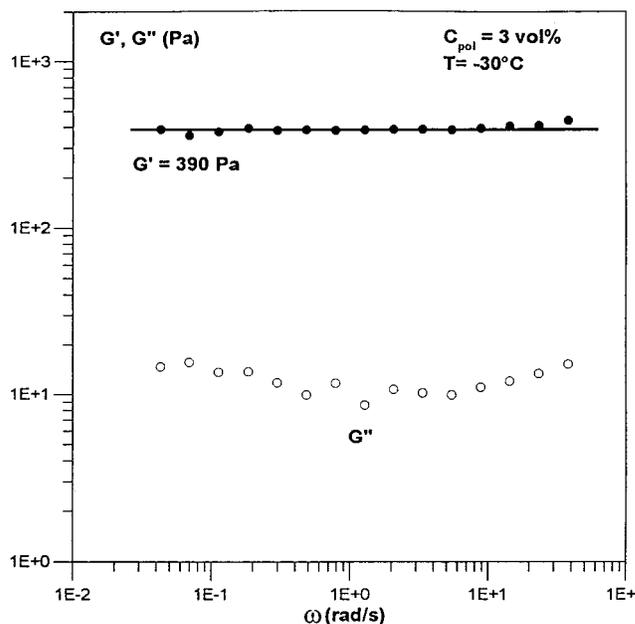


**Figure 6.** Dynamic moduli at  $-20\text{ }^{\circ}\text{C}$  for an EP copolymer ( $x_E = \text{mole fraction } 77.3\%$ ) gel prepared from a volume fraction 3% toluene solution.

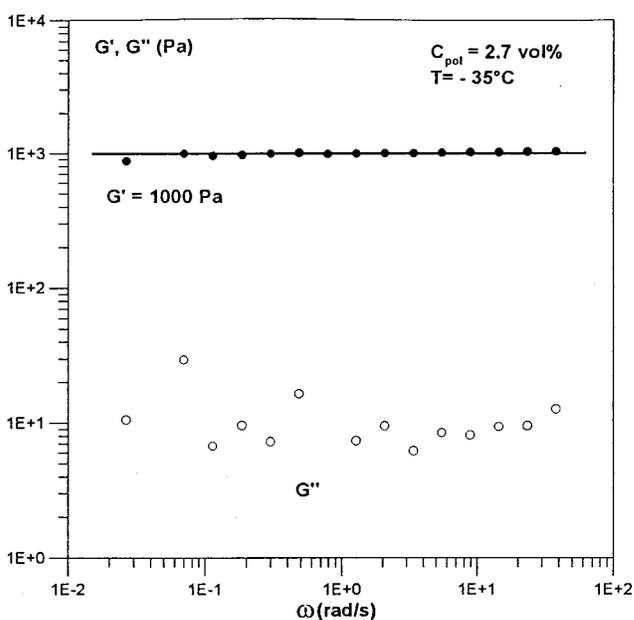


**Figure 7.** Dynamic moduli at  $-20\text{ }^{\circ}\text{C}$  for a EP copolymer ( $x_E = \text{mole fraction } 73.6\%$ ) gel prepared from a volume fraction 3% toluene solution.

where the value of  $m$  is equal to  $0.080 \pm 0.003$ . This relaxation behavior means that the connections between the fibers in the gel are weaker and more labile. This result is consistent with the SANS findings, which showed that when the ethylene content decreases the number of connections between fibers reduces. The dynamic moduli of the gel prepared from the volume fraction 3% mole fraction 73.6% EP copolymer in toluene were also measured at  $-30\text{ }^{\circ}\text{C}$ , and results are shown in Figure 8. At this temperature, however, the gel does not display any relaxation behavior since  $G'$  is relatively constant. These results clearly show the effect of the separation between the sol-gel transition temperature and the temperature at which the experiment is carried out. Increasing the separation decreases the frequency



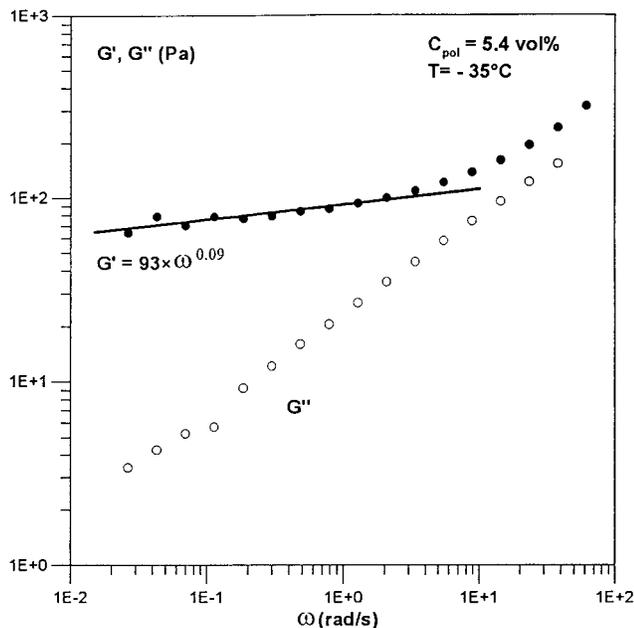
**Figure 8.** Dynamic moduli at  $-30\text{ }^{\circ}\text{C}$  for an EP copolymer ( $x_E = \text{mole fraction } 73.6\%$ ) gel prepared from a volume fraction 3% toluene solution.



**Figure 9.** Dynamic moduli at  $-35\text{ }^{\circ}\text{C}$  for an EP copolymer ( $x_E = \text{mole fraction } 77.3\%$ ) gel prepared from a volume fraction 2.7% methylcyclohexane solution.

dependency of the elastic modulus. The absence of a relaxation process at  $-30\text{ }^{\circ}\text{C}$  can be attributed to a larger amount of junctions formed between the polymer chains as the temperature further drops from  $-20$  to  $-30\text{ }^{\circ}\text{C}$ , making the cross-links between the fibers stronger.

Similar results were obtained in methylcyclohexane. Figure 9 shows the dynamic moduli at  $-35\text{ }^{\circ}\text{C}$  for a gel formed by the volume fraction 2.7% mole fraction 77.3% EP copolymer solution in methylcyclohexane. At this high ethylene content,  $G'$  remains constant for a wide range of frequencies and thus no relaxation behavior could be observed. However, Figure 10 shows that a relaxation process can be observed as in toluene when the ethylene content is decreased from mole fraction



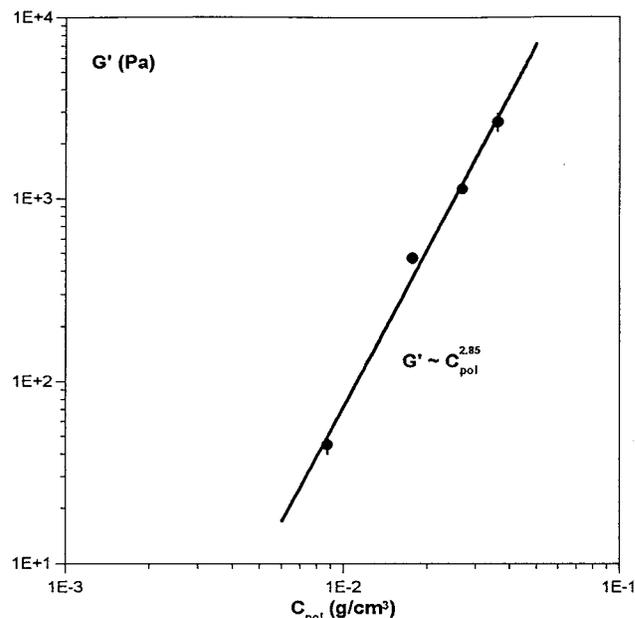
**Figure 10.** Dynamic moduli at  $-35\text{ }^{\circ}\text{C}$  for an EP copolymer ( $x_E = \text{mole fraction } 73.6\%$ ) gel prepared from a volume fraction 5.4% methylcyclohexane solution.

(77.3–73.6%). Here  $G'$  varies at low frequencies as  $\omega^m$  with a  $m$  value of  $0.09 \pm 0.01$ . It is noteworthy that the gel prepared from volume fraction 2.7% was weak and the experiment was difficult to carry out. So, it was carried out at a higher concentration of volume fraction, 5.4%. However, we expect an even bigger relaxation process with the gel prepared from a volume fraction 2.7% solution. On the other hand, measurements carried out at  $-45\text{ }^{\circ}\text{C}$  showed that decreasing the temperature increases the amount of connections between the fibers (results not shown). Indeed, at this temperature, we observed a variation of  $G'$  with  $\omega^m$  for a smaller  $m$  value of  $0.030 \pm 0.003$ . However, the gel still displays a relaxation behavior at this temperature, and the smaller  $m$  value suggests that the cross-links between the fibers are less labile as a consequence of more connections formed.

To gain a further understanding of the EP copolymer gel, we investigated the influence of the polymer concentration on viscoelastic properties. This study was limited to gel formed in toluene with the mole fraction 77.3% EP copolymer. Measurements were performed at  $-20\text{ }^{\circ}\text{C}$ , and no relaxation was observed. The variation of the elastic modulus as a function of the polymer concentration is shown in Figure 11. It can be seen that the variation of  $G'$  obeys the scaling law

$$G' \sim C_{\text{pol}}^{2.85 \pm 0.20} \quad (12)$$

We can examine this result using the theory developed by Jones and Marques for rigid gels.<sup>16</sup> This theory is based on the fractal dimension of the objects connected at the junctions of the network. Two types of elasticities are involved: entropic and enthalpic. Entropic elasticity occurs when connected objects can adopt different conformations, while enthalpic elasticity is related to the deformation of rigid objects, such as rod bending, whose conformation is frozen. Entropic elasticity ( $G_S'$ ) and enthalpic elasticity ( $G_H'$ ) are related to the network



**Figure 11.** Elastic modulus  $G'$  measured at  $-20\text{ }^{\circ}\text{C}$  vs polymer concentration for EP copolymer ( $x_E = \text{mole fraction } 77.3\%$ ) gels prepared from toluene solutions.

volume fraction  $\varphi$  by

$$G_S' = \varphi^{3/(3-D_f)} \quad \text{entropic} \quad (13)$$

$$G_H' = \varphi^{(3+D_f)/(3-D_f)} \quad \text{enthalpic} \quad (14)$$

where  $D_f$  is the fractal dimension of the objects connected between the junctions.

Our SANS experiment has shown that EP copolymer gels display a fiberlike structure. Thus, according to the theory of Jones and Marques, we should observe an exponent between 1.5 and 2 for a straight fiber possessing a longitudinal fractal dimension  $D_f = 1$ . This is not what we found. Instead, we found a significant discrepancy between the exponent of 2.85 found experimentally and a value between 1.5 and 2 predicted by the theory for a network composed of straight fibers. This difference can be explained if we consider the possibility that the fibers forming the network are not straight or nearly straight unlike most physical gels. An exponent of 2.85 would give a fractal dimension  $D_f = 1.95$  according to eq 13 or  $D_f = 1.44$  according to eq 14. Deviation of  $D_f$  from 1 suggests that the fibers formed in an EP copolymer gel are not straight. Though fiberlike gel has been observed for poly(vinyl chloride) (PVC) gels,<sup>17</sup> the fibers are not straight. In this case, the rectilinearity of the fibers is only achieved locally. For EP copolymer gels, the absence of straight fibers can be explained by the presence of the propylene units. EP copolymer chains are composed of straight, crystallizable sequences (ethylene units) alternating with more flexible sequences (propylene units). The presence of propylene units can disturb crystallization of ethylene units and prevent the formation of straight fibers.

## Conclusions

We have shown that EP copolymer gel displays a fiberlike structure. At a given temperature, the ethylene content has only a small effect on the diameter of the fibers formed in the gel but the amount of cross-links between the fibers is strongly dependent upon the

ethylene content. Viscoelastic data indicate that decreasing ethylene content increases the lability of cross-links in the network and confirm the neutron scattering findings. The viscoelastic data have also shown that elastic modulus and concentration follow a power law relationship. The exponent found in the power law suggests that the rectilinearity of fibers is achieved only locally. The absence of a long-range order due to the propylene units prevents the formation of straight fibers.

### References and Notes

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