Dispersion states of porous inorganic materials in polymer blends observed by inverse gas chromatography

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Inverse gas chromatography (i.g.c.) of columns prepared with a polymer blend of poly(ethylene oxide) (PEO) and polystyrene (PS) in the presence of pulverized porous inorganic materials has been studied. Information on the inorganics–polymer interaction was obtained from the change in the Z-shaped curve observed in the retention diagram. Inorganic materials except active carbon selectively incorporated PEO into their pores. The incorporation ability increased with increasing surface area of inorganic material. Molecular sieve 5A was scarcely able to incorporate PEO into its pores in spite of its large surface area, and this was ascribed to its small pore diameter. Active carbon selectively incorporated PS into its pores. Irreversible adsorption of a solute on active carbon was a dominant process in i.g.c. measurement for the column prepared with polymer and active carbon.

Keywords Inverse gas chromatography; porous inorganic materials; poly(ethylene oxide); polystyrene; polymer blend; dispersion state

INTRODUCTION

Inorganics–polymer interaction is a most interesting subject. Many studies have been made by various methods in order to develop new composite materials[1–10]. Inverse gas chromatography (i.g.c.) is a useful method to measure physical properties of a polymer, such as glass transition temperature and melting temperature[11]. I.g.c. has recently been used to characterize block or random copolymers[12–16]. By using i.g.c., we investigated the morphology of hydrophilic–hydrophobic polymer systems such as polymer blends of poly(ethylene oxide) (PEO) and polystyrene (PS)[17], poly(acrylic acid) and PS[18], and triblock copolymer of PEO and poly(methyl methacrylate)[19]. In the study of a polymer blend of PEO and PS, we clarified that even a slight change in surface structure of the polymer blend can be detected by i.g.c.[17]

The addition of porous inorganic material to the polymer blend of PEO and PS (PEO–PS blend) may bring about a change in its surface structure. This morphological change can be detected by an i.g.c. measurement, which will provide interesting information on the interaction between porous inorganic materials and polymers.

In this study we carried out i.g.c. measurements of columns prepared with PEO–PS blend and various porous inorganic materials. This paper describes the effect of pore structure of inorganic materials on the mutual interaction between polymers and porous inorganic materials.

EXPERIMENTAL

Materials

Wako Pure Chemical's PS ($M_n = 180000$) was purified by dissolving in benzene and precipitating into methanol. Both PS and PEO (Nakarai Chemical's PEO 6000, $M_n = 4600$) were freeze-dried from benzene solutions under vacuum and stored. Chromosorb P AW-DMCS 60–80 mesh (Johns-Manville Co., BET surface area 3 m^2 g^{-1}), which is a good solid support for i.g.c. measurements[20], was used as a support for the polymer. As a solute for gas chromatography, n-octane was used. The following inorganic materials were pulverized by dry-grinding in agate mortar for 1 h: active carbon (Mitsubishi Chemical's DIAHOPE 008, BET surface area 1280 m^2 g^{-1}), silica gel (Merck's silica gel 60, 537 m^2 g^{-1}), MS-5A (Nishio Industry's molecular sieves MS-5A, 457 m^2 g^{-1}), MS-13X (Yanagimoto Seisakusho's molecular sieves MS-13X, 436 m^2 g^{-1}), MgO (Konoshima Chemical's magnesia AR-H, 206 m^2 g^{-1}), γ-Al_2O_3 (self-made γ-alumina, 91 m^2 g^{-1}) and α-Al_2O_3 (self-made α-alumina, 2 m^2 g^{-1}).

Columns

The columns prepared in this series of experiments are summarized in *Table 1*. A certain amount of pulverized inorganic material was dispersed in a chloroform solution (2.5 w/v%) of PEO–PS blend by stirring sufficiently, and to this a prescribed amount of Chromosorb was added. The chloroform was allowed to evaporate at ambient temperature by gentle and continuous stirring of the solution followed by drying at 45°C under slightly reduced pressure. A weighed amount of Chromosorb prepared in this manner was tightly packed into a 1.5 m × 3 mm internal diameter stainless-steel column. The column was dried for 5 h at 45°C under a constant stream of helium.

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Measurements

The method of gas chromatographic measurement has been described in previous papers[17,20]. The measurement was carried out by increasing the column temperature T (K). The retention diagram (RD) was obtained by plotting log V_g *versus* $10^3/T$ (V_g is the specific retention volume of the solute: ml g^{-1}).

The specimen for scanning electron microscopy (SEM) was prepared by casting the polymer on a silane-treated glass plate[17] from a chloroform solution in which a small amount of pulverized inorganic material was suspended. The condition of SEM observation was identical to that employed in a previous work[17].

The BET surface area of each pulverized inorganic material was measured by one-point N_2-adsorption method using gas chromatography at liquid nitrogen temperature.

RESULTS AND DISCUSSION

Effect of surface area of inorganic materials

Figure 1 shows the effect of the amount of silica gel added to the PEO–PS blend on RD. Two Z-shaped curves were observed in the RD for the column prepared without additive (no. 1 in *Table 1*). As previously reported, the one observed at temperatures around 60°C is attributed to the melt transition of PEO and the other around 95°C is due to the glass transition of PS[17]. The depth of the Z-shaped curve observed around the melting temperature (T_m) of PEO decreased with an increase in amount of silica gel and was almost unobservable in the RD for column no. 5 (3.8 wt% addition), while unremarkable change was observed in the Z-shaped curve observed around the glass transition temperature (T_g) of PS. Further, the value of V_g at a certain column temperature increased with the increasing amount of silica gel, that is, an upward shift of RD was observed.

In *Figure 2* is shown the effect of the kind of additive to the PEO–PS blend with low concentration (0.5 wt%) on

Table 1 Columns for gas chromatography

	Polymer		Additive		
Column no.	Sort[a]	Loading[b] (wt%)	Sort	BET surface area ($m^2 g^{-1}$)	Loading[c] (wt%)
1	PEO–PS	9.2	–	–	–
2		9.4	Active carbon	1280	0.5
3		9.7	Silica gel	537	0.5
4		9.6	Silica gel	537	1.8
5		9.3	Silica gel	537	3.8
6		9.6	MS–5A	457	3.8
7		9.5	MS–13X	436	3.8
8		9.8	MgO	206	0.5
9		9.5	MgO	206	3.8
10		9.6	γ–Al_2O_3	91	3.8
11		9.3	α–Al_2O_3	2	3.8
12		5.0	–	–	–
13		10.0	–	–	–
14		5.0	Silica gel	537	3.8
15		9.9	Silica gel	537	0.5
16		9.6	Silica gel	537	3.8

[a] PEO–PS: polymer blend of PEO and PS (1:1 mixture in weight)

[b] Polymer (g)/[additive(g) + polymer(g) + Chromosorb(g)] x 100

[c] Additive(g)/[additive(g) + polymer(g) + Chromosorb(g)] x 100

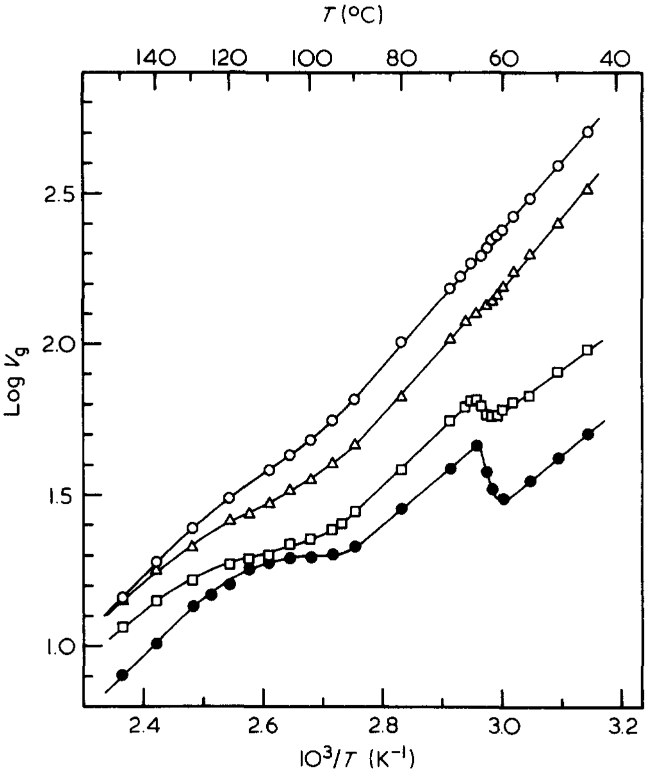

Figure 1 Effect of silica gel amounts added to the PEO–PS blend on retention diagram: ○, column no. 5 (3.8 wt%); △, no. 4 (1.8 wt%); □, no. 3 (0.5 wt%); ●, no. 1 (without additive)

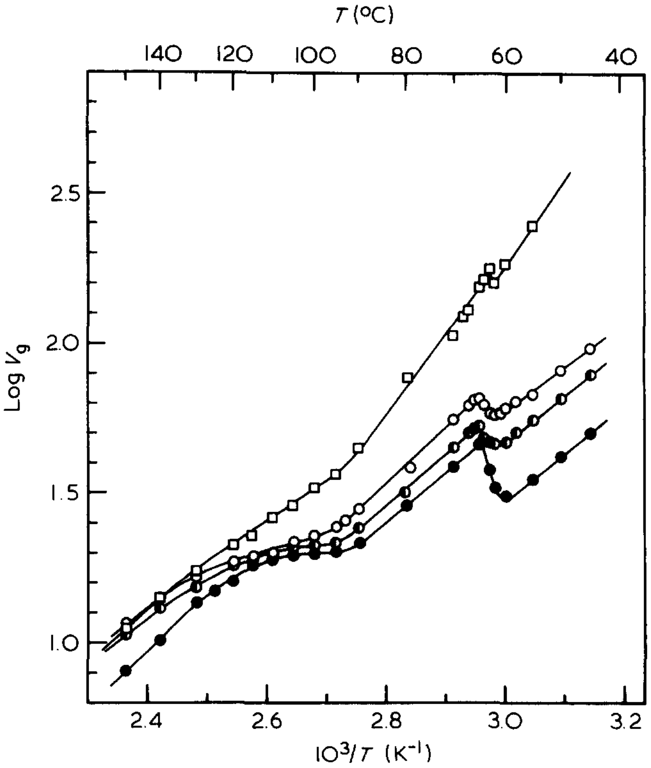

Figure 2 Effect of kind of additive with low concentration (0.5 wt%) added to the PEO–PS blend on retention diagram: □, column no. 2 (active carbon); ○, no. 3 (silica gel); ◐, no. 8 (MgO); ●, no. 1 (without additive)

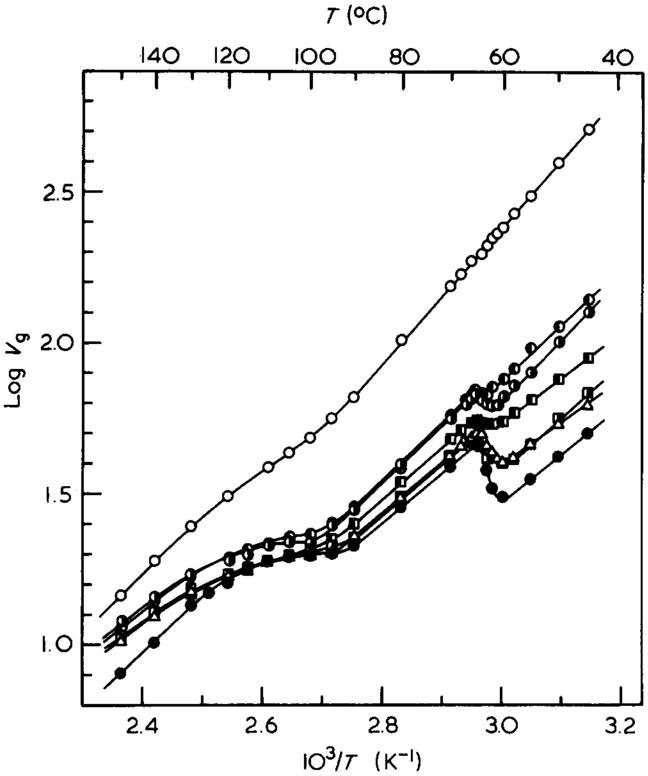

Figure 3 Effect of kind of additive with high concentration (3.8 wt%) added to the PEO–PS blend on retention diagram: ○, column no. 5 (silica gel); ◐, no. 9 (MgO); ◑, no. 7 (MS–13X); ◧, no. 10 (γ–Al_2O_3); ◨, no. 6 (MS–5A); △, no. 11 (α–Al_2O_3); ●, no. 1 (without additive)

RD. The depth of the Z-shaped curve observed around T_m of PEO decreased and also RD shifted upwards with an increase in surface area of inorganic material. Essentially the same tendency described above was also observed in the case of higher concentration of additives (3.8 wt%) as shown in *Figure 3*. However, the addition of MS-5A or MS-13X resulted in retention diagrams (RDs) which deviated from this tendency. In spite of their large surface areas the RDs of MS-5A and MS-13X almost overlapped with those of α-Al_2O_3 and MgO, respectively. In an i.g.c. measurement of the column prepared with 3.8 wt% addition of active carbon, the solute peak did not appear at any column temperature.

The SEM photographs of cast films of PEO–PS blend prepared in the presence of porous inorganic materials are given in *Figure 4*. It was found from a previous result[17] that the PS and PEO domains formed the sea and island phases, respectively, in photographs (a) and (b). Active carbon was present in the PS domain, and silica gel in the PEO domain. In the case of other inorganic materials, essentially the same pictures as in the case of silica gel were obtained. Thus the inorganic materials except active carbon were present in the PEO domain.

To explain these results a model for adsorption sites for n-octane was proposed and is shown in *Figure 5*. Three sites are important in the retention mechanism: the surface of polymer which covers the Chromosorb surface (site A); the uncovered surface of porous inorganic material (site B); the polymer-covered part of porous inorganic material where all the pores are filled with polymer (site C). As the surface area of polymer at site A is much larger than that at site C, the adsorption–desorption of n-octane at site A mainly governs the retention mechanism. The increase in surface area or in amount of addition of porous inorganic material results in the increase in the amount of polymer incorporated into the pore of inorganic material at site C. This increase will bring about the decrease in the amount of polymer at site A. As shown in *Figure 4*, in PEO–PS blend, inorganic materials except active carbon selectively incorporate PEO into their pores. Therefore, except in the case of active carbon, the amount of PEO at site A decreases with increasing surface area or amount of inorganic material, whereas the amount at site A is constant. It is reasonable to consider that the decrease in the depth of the Z-shaped curve observed around the T_m of PEO with increasing surface area or amount of addition of porous inorganic material was responsible for the decrease in the amount of PEO at site A because of the incorporation of PEO into the pores of the inorganic material at site C. The Z-shaped curve observed around the T_g of PS was not changed so greatly by the additives, which is ascribed to the constant amount of PS at site A and to the insensitivity of the Z-shaped curve around the T_g of PS to the composition of PEO–PS blend as previously reported[17].

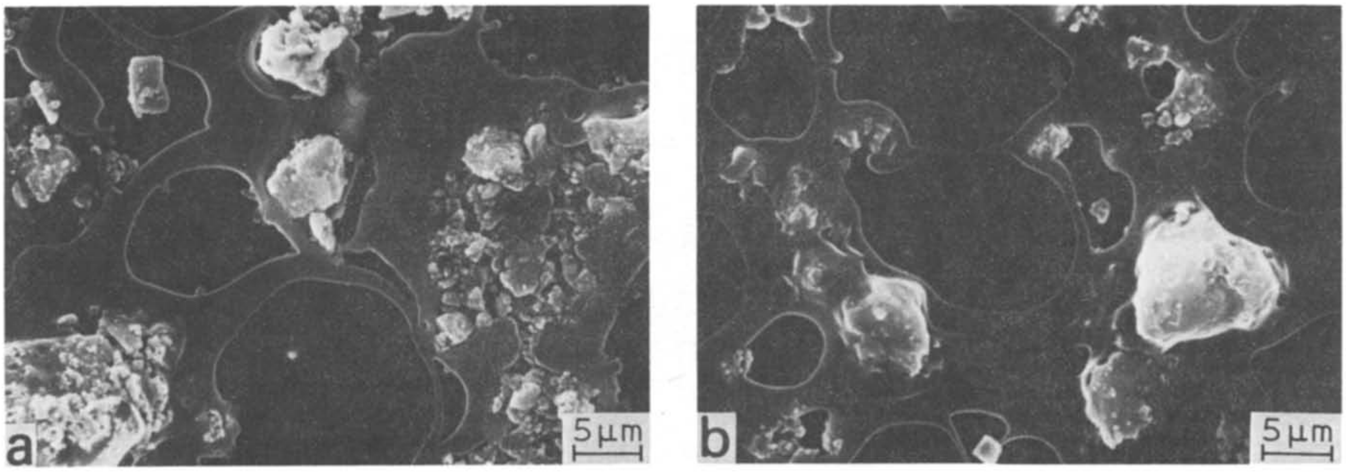

Figure 4 SEM photographs of PEO–PS blend cast from $CHCl_3$ in the presence of inorganic materials: (a) silica gel, (b) active carbon

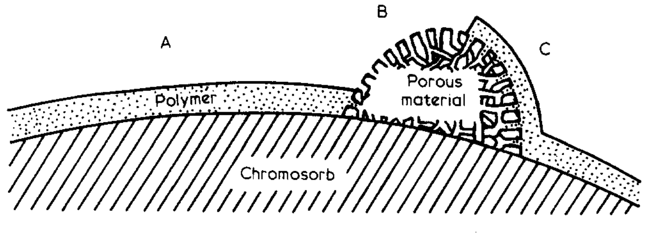

Figure 5 A model for adsorption sites for n-octane

The increase in surface area or amount of addition of porous inorganic material will also result in the increase in the surface area of site B. In such a case, the adsorption–desorption at site B should affect the retention mechanism because of strong adsorption on the inorganic material. As can be seen from *Figures 1, 2* and *3*, the increase in the amount or the surface area of the additive also resulted in the upward shift of RD, which is considered to be attributed to the increase in the surface area of site B, which means occurrence of stronger adsorption of n-octane.

Effect of pore diameter of inorganic materials

As shown in *Figure 3*, the addition of molecular sieves to the PEO–PS blend gave exceptional RDs. In the case of MS-5A, its pore diameter (5 Å) was too small to incorporate the chloroform solution of PEO, and PEO widely covered the surface of MS-5A. Therefore, the surface area of site B was fairly small and the amount of PEO at site A did not decrease so greatly. Because of these phenomena the RD in the case of MS-5A addition almost overlapped with that of α-Al_2O_3 (surface area 2 $m^2\ g^{-1}$) addition in spite of its large surface area (457 $m^2\ g^{-1}$). In the RD of MS-13X addition, whose pore diameter (10 Å) is somewhat larger than that of MS-5A, the decrease in the depth of the Z-shaped curve observed around T_m of PEO and the upward shift of RD were much more easily observed in comparison with the RD of MS-5A addition. It can be regarded, therefore, that PEO was incorporated into the pore of MS-13X to some extent, and accordingly the surface area of site B increased and the PEO amount at site A decreased. The RD of MS-13X (436 $m^2\ g^{-1}$) addition, however, was roughly identical to the RD of MgO (206 $m^2\ g^{-1}$) addition, which indicates that polymer solution was not sufficiently incorporated into the pore of MS-13X.

Effect of irreversible adsorption

The interpretation described above cannot be applied to the result for active carbon addition. Active carbon has an affinity for PS as shown in *Figure 4*. PS was incorporated into the pore of active carbon and the amount of PS at site A decreased. Accordingly, as can be seen from *Figure 2*, the Z-shaped curve around the T_g of PS in the RD of active carbon addition appeared less distinct than that in the RDs for the other columns. Since the decrease in the PEO amount at site A would be negligible, the depth of the Z-shaped curve around the T_m of PEO in the RD of active carbon addition should be identical to that without additive. In practice, however, the depth was appreciably decreased. The adsorption on active carbon is very strong and especially irreversible adsorption occurs. As the extent of irreversible adsorption of n-octane at site B was large, the amount of n-octane which contributes to the adsorption–desorption at site A decreased, and this led to the decrease in the depth of the Z-shaped curve at T_m of PEO. The strong irreversible adsorption at site B also brought about the upward shift of RD. The validity of this explanation was supported by the fact that the solute peak did not appear in i.g.c. measurement of the column prepared with 3.8 wt% addition of active carbon.

Incorporation of PEO into the pore of silica gel

In *Figure 6* are shown the RDs for columns no. 12–16, in which PEO–silica gel or only PEO was loaded on the Chromosorb. In the RDs of the same PEO loadings, the increase in the amount of silica gel addition resulted in both the upwards shift of RD and the decrease in the depth of the Z-shaped curve, as was expected from the discussion described above.

The Z-shaped curve was not observed in the RD for column no. 14 (5 wt% PEO, 3.8 wt% silica gel) in which 0.242 g of PEO and 0.184 g of silica gel were packed. As the density of PEO is 1.22 g cm^{-3} and the pore volume of silica gel is 0.4 $cm^3\ g^{-1}$,[21,22] 0.184 g of silica gel is capable of incorporating 0.090 g of PEO into the pore. It is the question whether residual PEO (0.152 g) existed at site A or at site C. In this case 0.152 g of PEO corresponds to 3.1 wt% PEO. As previously reported, a Z-shaped curve was not observed in the RD for the column prepared with PEO loading less than 5.0 wt%[17]. Therefore, it is reasonable to consider that the PEO corresponding to 3.1 wt%

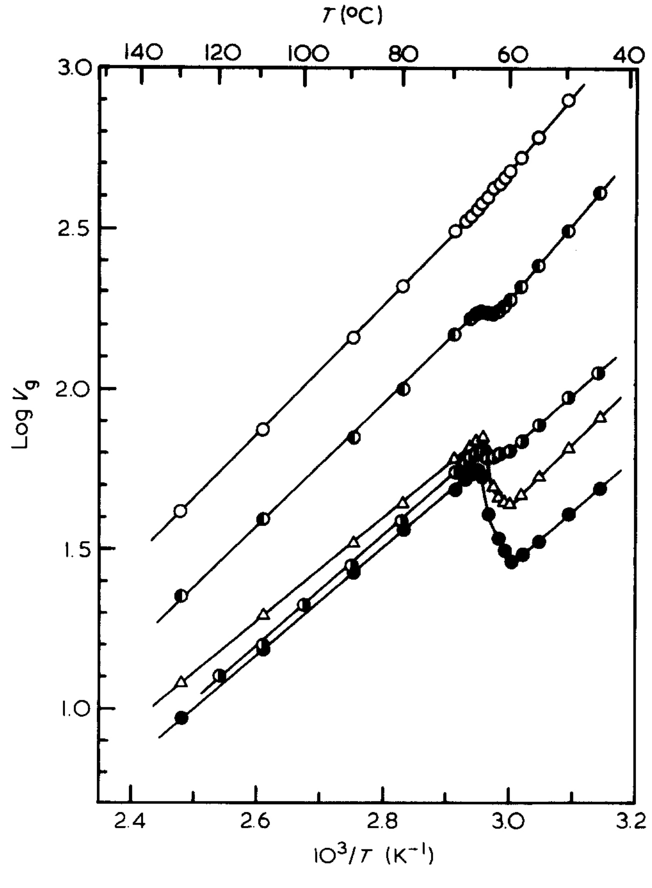

Figure 6 Effect of silica gel amounts added to PEO on retention diagram: ○, column no. 14 (5.0 wt% PEO, 3.8 wt% silica gel); ◐, no. 16 (9.6 wt% PEO, 3.8 wt% silica gel); ◑, no. 12 (5.0 wt% PEO, without additive); △, no. 15 (9.9 wt% PEO, 0.5 wt% silica gel); ●, no. 13 (10.0 wt% PEO, without additive)

(0.152 g) did not contribute to the appearance of the Z-shaped curve and the residual PEO existed mainly at site A. Although the residual PEO might exist partly at site C, the amount should be very small. In column no. 16 (9.6 wt% PEO, 3.8 wt% silica gel), 0.466 g of PEO and 0.184 g of silica gel were packed. As 0.184 g of silica gel can incorporate 0.090 g of PEO into its pore, about 0.37 g of PEO existed at site A which corresponds to 7.7 wt% PEO. The depth of the Z-shaped curve for the column prepared with 7.7 wt% PEO is expected to be roughly the same as that prepared with 5.0 wt% PEO. As can be seen from *Figure 6*, the depth of the Z-shaped curve in the RD for column no. 16 was nearly the same as that for column no. 12 (5.0 wt% PEO, without additive). Accordingly, the discussion described above is reasonable.

It should be noted that these quantitative interpretations may be varied somewhat by the difference in the molecular weight of polymers employed. However, the qualitative behaviour should be fundamentally the same as described above.

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