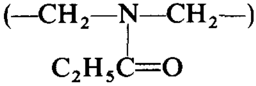
Intermacromolecular complexes by *in situ* polymerization

Fu-Lung Chen, E. M. Pearce and T. K. Kwei*
Chemistry Department, Polytechnic University, Brooklyn, New York, USA and
Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan
(Received 15 April 1988; revised 6 June 1988; accepted 7 June 1988)

Hydrogen-bonded complexes of poly(acrylic acid) and poly(ethyl oxazoline) (PEOx) were prepared by photopolymerization of acrylic acid in which PEOx was dissolved. The glass transition temperatures (T_g) of the complexes are not only higher than those of the blends but also higher than the T_g value of either component polymer. The complexes dissolve in strong proton-accepting solvents like dimethyl formamide or dimethyl sulphoxide (DMSO), are swollen to various degrees in water and methanol, but are resistant to swelling by dioxane. When the density of hydrogen bond donor groups in the chain is reduced by 50% with the use of a copolymer of acrylic acid and methyl methacrylate, intermolecular association still takes place, although the affinity of complexation is reduced to some extent. When interpenetrating networks (semi-IPNs) are prepared by this method, about half of the PEOx can be extracted by DMSO after 4 days. The incomplete removal is probably a result of topographical constraints against diffusion.

(Keywords: complexes; poly(acrylic acid); poly(ethyl oxazoline))

INTRODUCTION

Macromolecules with complementary binding sites associate in solution to form intermolecular complexes[1,2]. In a previous publication[3], experimental observations on the formation of hydrogen-bonding complexes between poly(acrylic acid) and poly(ethyl oxazoline) (PEOx),  $(-CH_2-\underset{\underset{C_2H_5C=O}{|}}{N}-CH_2-)$, were reported. Mutual precipitation occurred in water, methanol and dioxane solutions and the compositions of the precipitates corresponded to molar ratios of 2/3, 3/4, 0.9 from water, 1/2, 2/3, 1/1 from methanol, and 1/1, 2/1, 0.83 from dioxane. However, these compositions are in general not the same as feed compositions. Furthermore, the precipitates obtained from the three solvents had different compositions even when the same feed composition was used.

Another observation of interest concerns the glass transition temperatures (T_g) of the complexes. Each precipitate exhibited a single T_g. The three precipitates from water had T_g values of 115, 115 and 110°C, respectively, all three values being higher than the T_g values of PEOx, 55°C, and PAA, 104°C. The precipitates from methanol had T_g values of 107, 105 and 95°C. The first two values are about the same as the T_g of PAA while the last value is much higher than the weight-average value of the T_g values of the component polymers. The complexes obtained from dioxane however, had entirely different T_g values. They had the same T_g of 71°C although their compositions varied from 45.6 to 66.5 mol% PEOx. Clearly, the nature of the solvent exerted a profound influence on interpolymer association, as had been pointed out in reviews by Tsuchida and Abe[1], and by Bekturov and Bimendina[2].

A natural extension of the above study is to prepare complexes in the absence of solvent. Mixing the two polymers in the melt is not suitable in this case because PAA undergoes anhydride formation at temperatures above 150°C. Therefore, we have opted to photopolymerize acrylic acid in which PEOx is dissolved. The solubilities and the T_g values of the complexes and interpenetrating polymer networks prepared by *in situ* polymerization are reported here. Preliminary results on complexation between PEOx and acrylic acid–methyl methacrylate copolymers using the same method of preparation are also presented.

EXPERIMENTAL

Materials

PEOx from Dow Chemical Co., with a reported molecular weight of 50 000, was purified by filtration of dichloromethane solution prior to precipitation into a large volume (10:1) of hexane. The precipitate was dried under vacuum at 80°C for 3 days.

Chemicals

Acrylic acid and benzoin methyl ether (photoinitiator) were obtained from Aldrich Chemical Co. with reported purities of 99% and 97%, respectively. The crosslinking agents used in the synthesis of interpenetrating networks (IPNs) were diethylene glycol diacrylate and 1,1,1-trimethylolpropane triacrylate from Polyscience Inc. These chemicals were used without purification. The solvents dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF) were distilled before use.

Preparation of complexes and semi-IPNs

After dissolution of PEOx in acrylic acid (AA), 0.5 wt% of benzoin methyl ether with respect to acrylic acid was added to the solution which then was cast onto a Teflon plate and covered with a thin polyethylene film which served to minimize the loss of monomer due to evaporation and to reduce the inhibitory effect of oxygen during photopolymerization. The cast solution was exposed to a long wavelength u.v. lamp (Black-Ray model B-100A) for 3–5 min during which acrylic acid was

---

* To whom correspondence should be addressed

0032-3861/88/122285-05$03.00

Table 1 Solubilities of PEOx–PAA complexes

Molar ratio PEOx/PAA	Dioxane	Water		Methanol		DMF	DMSO
		Film	Solution	Film	Solution		
1:2.03	No visible change	Swollen	Clear	Swollen sticky	Clear	Dissolved	Dissolved easily
1:2.66	No visible change	Swollen	Clear	Swollen sticky	Clear	Dissolved	Dissolved easily
1:3.95	No visible change	Swollen, break up to spherical particles	Hazy	Swollen sticky	Clear	Dissolved	Dissolved easily
1:5.21	No visible change	Change to white powder	Very hazy	Change to swollen powder	Very hazy	Dissolved	Dissolved easily
1:7.62	No visible change	Change to white powder	Very hazy	Change to swollen powder	Very hazy	Dissolved	Dissolved easily

Table 2 Compositions of the complexes before and after extraction

	Composition (molar ratio PEOx/PAA)				
Sample	1	2	3	4	5
As prepared	1:2.03	1:2.66	1:3.95	1:5.21	1:7.62
After water extraction	1:1.83	1:1.83	1:1.84	1:2.64	1:4.14
After methanol extraction	1:1.86	1:2.25	–	1:2.37	–
After dioxane extraction	1:2.01	–	–	–	1:7.66

polymerized to high conversions. The complexes were dried under vacuum at 93°C for 3 days and then at 100°C for 1 day. These temperatures were chosen to avoid anhydride formation in PAA. The semi-IPNs were prepared by the same method except that a mixture of the diacrylate and triacrylate (3/2) was used as cross-linking agent. The compositions of the complexes and IPNs were determined by elemental analysis before and after solvent extraction.

Solubility and extraction experiments

The complexes after drying were immersed in water, methanol, dioxane, DMF and DMSO solvents for 4 days in order to test for solubilities. The semi-IPN specimens were extracted by DMF and DMSO. The samples were dried to constant weight after extraction.

Determination of T_g

The T_g values of the complexes and IPNs were determined with the use of a DuPont 9900 differential scanning calorimeter. About 10 mg of each sample was placed in a pierced-lid aluminium pan. Typical procedures were as follows: first, the sample was heated at 50°C min^{-1} to 150°C and held at that temperature for 5 min followed by cooling at about 70°C min^{-1} to 40°C. This procedure ensured that the samples were solvent free and had the same thermal history. Next, the sample was reheated at 10°C min^{-1} to 150°C. The T_g was taken as the onset of the abrupt increase in the heat capacity of the specimen. The T_g values are reproducible to about $\pm$1.0°C. The midpoint of the change in specific heat was also recorded for the purpose of comparing the 'width', i.e., the temperature span, of the transition.

RESULTS AND DISCUSSION

Physical properties of the complexes

In the preparation of PEOx–acrylic acid solutions, it was found that only the mixtures containing less than $\sim$40% wt% PEOx were convenient for handling. Therefore we prepared five complexes containing 40.3, 34.0, 25.8, 20.9 and 15.3 wt% PEOx, respectively. The solubilities of these complexes increased in the order: dioxane < water < methanol < DMF < DMSO, as shown in *Table 1*. It was readily noted that strong proton accepting solvents, DMF and DMSO, dissolved the complexes. This observation is in complete accord with earlier findings that mutual precipitation does not occur in either solvent. Dioxane, on the other hand, caused no visible changes in the appearances of the complex films. Water and methanol did not dissolve the complexes but had stronger solvating power than dioxane. The films became swollen and in some instances broke up into powdery particles. In these mixtures, the 'solution' phase above the powdery particles was turbid but could be filtered through a 0.45 filter, to result in a clear solution. The quantity of the suspended particles was small in each case.

The compositions of the complexes before and after extraction by dioxane, water and methanol are listed in *Table 2*. Immersion of samples 1 and 5 in dioxane for 4 days resulted in no change in composition. Apparently all the polymer species are associated, at least to some extent, to result in complete insolubility in dioxane. The solubility characteristic of sample 5 is of particular interest. With a PEOx/PAA ratio of 1:7.6, it contains a large excess of the latter polymer, and the average number of hydrogen bonds per carboxyl group cannot exceed 0.13 even if every amide group in PEOx is assumed to be engaged in hydrogen bonding. The small number of contacts per carboxyl group already suffices to render the complex insoluble in dioxane. On the other hand, extraction with water yielded different results. The composition of the water insoluble material became 1:4.1, indicative of partial dissolution of the PAA component. A possible interpretation of this observation is that there is a distribution of the number of hydrogen bonds per PAA molecule in the photopolymerized complex and PAA molecules having a low degree of association with PEOx are soluble in water. We did not

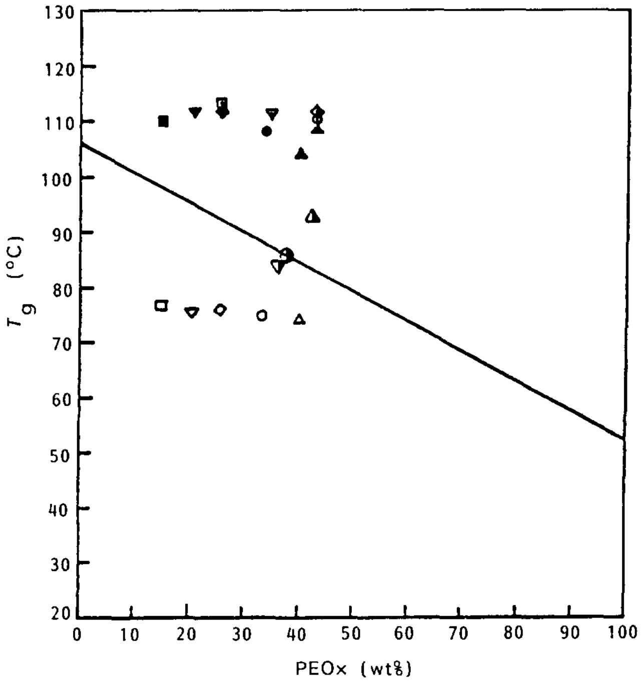


Figure 1 Glass transition temperatures of as-polymerized PEOx–PAA complexes (solid symbols); film cast after dissolving in DMSO (open symbols); extracted by methanol (half-filled symbols) and extracted by water (symbol with dot inside)

analyse the clear solution to determine whether the weakly associated PAA chains carried PEOx molecules into solution. It can be readily calculated from material balance that the soluble material contains at least 12 times more PAA (moles) than PEOx and, as a first approximation, we need to consider only PAA as the dissolved species.

Just as the mutual precipitates from solution do not have a single composition[3], the insoluble fractions from the five samples likewise do not have a common composition. For example, the PEOx/PAA ratio of sample 4 is 1:5.2. Although the PAA content is higher than that of the water insoluble fraction of sample 5, (1:4.1) the composition after extraction is only 1:2.6. It appears that sample 4 has a distribution of degree of association different from that in sample 5, which is reflected in the composition after extraction. The same reasoning can be used to rationalize the results obtained for the other water (or methanol) extraction experiments.

The water insoluble fractions of samples 1, 2 and 3 have the same composition, a ratio of 1:1.8. Coincidentally the methanol insoluble fraction of sample 1 also has the same molar ratio. When taken together with the moderate extent of swelling seen in solubility tests, these results are suggestive of a high degree of association present in these materials.

There is an important difference between the results of this study and those of mutual precipitation experiments. In the latter experiments, the compositions of the precipitates corresponded, in most cases, to simple molar ratios of 2:1, 3:4, 2:3, 1:1 and 1:2. These exact ratios were not found in water and methanol insoluble materials. The disparity can be understood if one considers the dynamics of the polymerization process. As acrylic acid monomer is converted to its polymer, the PAA chains formed at the early stages of polymerization are likely to have ample opportunity to establish a large number of contacts with PEOx. However, chains formed at later stages are apt to have fewer amide groups available for hydrogen bonding or have low segmental mobility, due to vitrification of the mixture, which limits the extent of bonding for kinetic reasons. This leads to a distribution of the degree of association for PAA chains and those with a degree of association lower than a certain critical value entered in solution. The fraction of PAA molecules having a degree of association higher than a critical value for insolubility can vary from one sample to another. (The critical value, of course, depends on the solvent power.) Since all PAA chains having degrees of association higher than a critical value are insoluble according to this interpretation, the overall compositions of the insoluble fractions do not conform to simple stoichiometries.

The T_g of PAA was determined to be 106°C and that of PEOx, 52°C. The photopolymerized mixtures had T_g values ranging from 106 to 113°C, as shown in *Figure 1*. The same high T_g values were obtained for mutual precipitates from water[3]. (In this connection, several other hydrogen-bonded complexes also exhibited high T_g values[4–9]). When these materials were dissolved in DMSO and films were then cast from solutions, the T_g values became markedly lower. The low T_g values of solution cast films, also shown in *Figure 1*, agree generally with earlier results[3]. Although the possibility of residual DMSO trapped in the film cannot be dismissed, the low T_g values are still believed to be qualitatively valid[5].

Extraction with dioxane did not alter the T_g values of samples 1 and 5. This is understandable because the compositions remain unchanged. Extraction by water resulted in insoluble materials richer in PEOx content than the originals, and the T_g values were either unchanged or became marginally higher, by 3–5°C. The results of methanol extraction however, were completely different. The insoluble fractions had lower T_g values. The decreases were 12, 22 and 28°C for samples 1, 2 and 4. Additional differences came to our attention in that the 'width' of the glass transition as manifested in a differential scanning calorimetry experiment was much larger in the methanol-insoluble material. Thus, the temperature spans between the onsets (extrapolated) and the midpoints of the specific heat jumps were between 5.5 and 8.5°C for the as-polymerized complexes and for dioxane- or water-insoluble fractions, but increased to 16–18°C in methanol-extracted fractions. If the high T_g values of the as-formed complexes and the water insoluble fractions could be attributed to a high degree of association, the low T_g values of the methanol-insoluble fractions would mean that the degree of association had diminished by the methanol extraction process. Since methanol was a more powerful swelling agent than water it was possible that not all the hydrogen bonds were re-established during drying once the complexes were highly swollen. In support of this interpretation were the broader temperature spans of the glass transitions which could be viewed as manifestations of broader distributions of the degrees of hydrogen bonding. The correlation between the width of glass transition and the extent of hydrogen bonding was found in other blends[10].

Acrylic acid copolymers as hydrogen bond donors

In the second phase of this work we attempted to study how complexation was modified by decreasing the

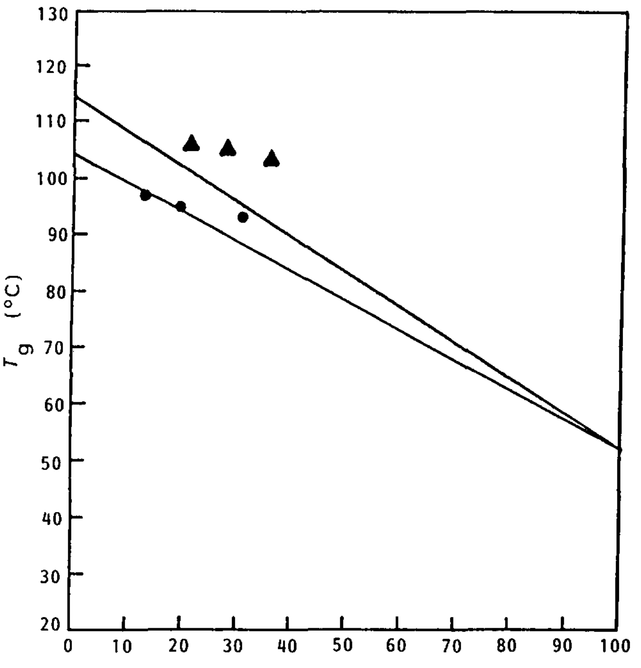


Figure 2 Glass transition temperatures of PEOx–PAA50 (●) and PEOx–PAA80 (▲)

density of proton-donating groups in the chain. To this end, we employed mixtures of acrylic acid and methyl methacrylate monomers in our photopolymerization experiments. Only two copolymer compositions were used and the resulting complexes were designated as PEOx–PAA50 and PEOx–PAA80 with the numerals representing the mole per cent of the acrylic acid in the copolymer. Since there is a large disparity in monomer reactivity ratios, the sequence distribution is not random. Therefore we did not investigate the composition changes caused by extraction with dioxane. Only visual observations are reported here. The three complex films of PEOx–PAA80 having PEOx/AA ratios of 1:1.8, 1:2.6 and 1:3.7 were not swollen by dioxane and the solutions were clear. The complex film of PEOx–PAA50 having a PEOx/AA ratio of 1:1.3 likewise did not swell, but the two other films having ratios of 1:2.4 and 1:3.8 were swollen and the solutions were hazy. Thus, complex films derived from PAA80 were resistant to swelling by dioxane, as in the case of PAA homopolymer. But as the carboxyl content decreases to 50% in PAA50, the complexes became more susceptible to swelling by dioxane, due to the presence of methacrylate units.

The T_g values of PEOx–PAA80 complexes were all higher than the weight-average values. The positive deviation ranged from 5 to 11°C. The transition temperatures of PEOx–PAA50 complexes, on the other hand, were close to weight-average values (*Figure 2*). The hydrogen bonding contribution to T_g was larger in PEOx-PAA80 than in PEOx-PAA50 when data were compared either at comparable PEOx contents or PEOx/AA ratios. The affinity of complexation is apparently reduced, by the MMA units in the copolymer.

Extraction by dioxane did not change the T_g values of PEOx–PAA80 complexes. The transition temperature of PEOx–PAA50 complex having a PEOx/AA ratio of 1:1.3 also remained the same but the T_g values of the other two complexes decreased by 2 and 4°C, respectively. The results are consistent with the solubility characteristics of these films.

Interpenetrating networks

The third phase of this study is concerned with the effect of crosslinking on the properties of complexes. Three semi-IPNs were prepared, using 2.5, 5.0 and 10.0 wt% (based on acrylic acid) of the crosslinking agents. The swelling ratios of these materials in water were determined to be 1.8, 1.7 and 1.5, respectively. The decrease in swelling ratio with the amount of crosslinking agent was linear. The losses in the weights of the three networks due to extraction were 2.2, 1.9 and 1.2%, again decreasing linearly with the amount of crosslinking agent. Since the weight losses were small, only the compositions after extraction are shown in *Table 3*. The T_g values of the three networks were between 107°C and 111°C. After water extraction, the T_g increased by 2, 5 and 7°C, respectively, the increase being larger for more densely crosslinked materials. Since it is improbable that the removal of 1% of soluble material from network 3 can account fully for the 7°C increase, a more likely explanation is that swelling by water allows additional carboxyl and amide groups to rearrange themselves with the desired juxtaposition for hydrogen bonding. The rearrangement effect is more pronounced at high crosslink density because there is relatively more relief from the frozen-in configurations in the densely crosslinked network.

Experiments were also carried out to see if PEOx molecules could be extracted from the network by strong solvents such as DMF and DMSO. The weight loss due to DMSO extraction was determined after immersion in solvent at ambient temperature for 10, 20, 50 and 96 h. The results of DMSO extraction are shown in *Figure 3*. The weight loss after DMF extraction is smaller but the curves have the same shapes and therefore are not shown. For the two highly crosslinked networks, the weight losses reached limiting values after 2 days. For the network having the lowest crosslinking density, there appeared to be a continuing decrease in weight after 4 days. The compositions of the extracted materials deduced from mass balance are shown in *Table 3*. A small

Table 3 Properties of semi-interpenetrating polymer networks (semi-IPNs)

	Semi-IPNs		
	1	2	3
Crosslinking agent (wt%)[a]	2.5	5.0	10
Swelling ratio (water)	1.8	1.7	1.5
Weight loss after 4 day water extraction (%)	2.2	1.9	1.2
Composition after water extraction, PEOx/PAA	1:2.57	1:2.55	1:2.46
T_g before water extraction (°C)	111	108	107
T_g after water extraction (°C)	113	113	114
PEOx in DMSO extract (wt%)[b]	47.2	42.4	37.0
PAA[c] in DMSO extract (wt%)[d]	4.3	0	0

[a] Weight percentage is based on the weight of acrylic acid

[b] Weight percentage is based on the weight of PEOx in PEOx–PAA semi-IPN before extraction

[c] Where the PAA contains crosslinking agents

[d] Weight percentage is based on the weight of PAA in PEOx–PAA semi-IPN before extraction

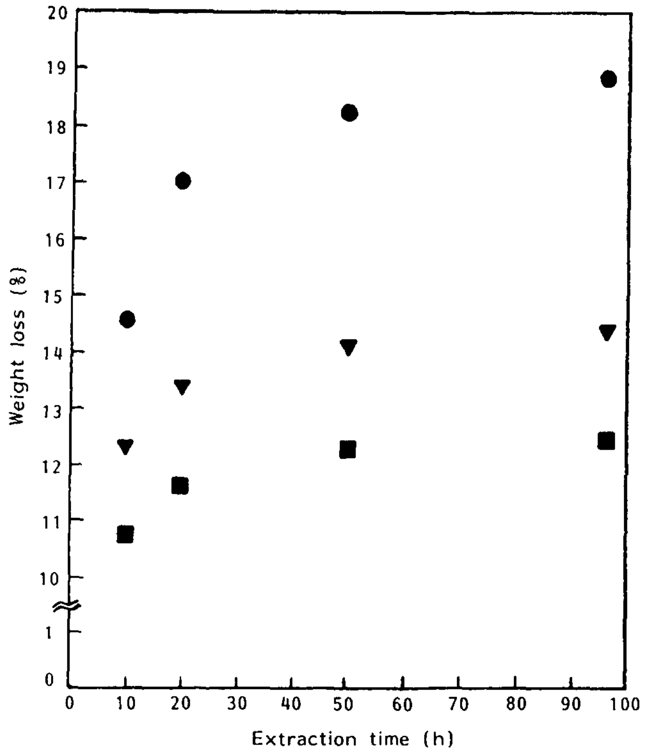


Figure 3 Weight loss due to extraction by DMSO at various extraction times for the PEOx–PAA semi-IPNs with 10 wt% (■); 5 wt% (▼) and 2.5 wt% (●) of crosslinking agents

quantity of PAA, about 4.3%, was lost from the network containing 2.5% crosslinking agent, but none appeared in the extractables of the other two semi-IPNs. The major component of the soluble material was PEOx, as expected, but more than half of the PEOx was not extracted, probably due to topographical constraints against diffusion.

CONCLUSIONS

The following conclusions are reached from the results of this study. *In situ* photopolymerization of AA in the presence of PEOx can be used to prepare PEOx–PAA complexes. The T_g values of the PEOx–PAA complexes prepared by this procedure are much higher than those of the blends and the high values can be attributed to hydrogen bonding acting as physical crosslinks. The solubility of complex in solvents decreases in the order of DMSO > DMF > methanol > water > dioxane. The solvents with equal or stronger proton-accepting ability than PEOx can dissolve the PEOx–PAA complexes. The complexes are swollen, to various degrees, in both water and methanol, but are not attacked by dioxane. Complexes of PEOx–PAA80 are resistant to dioxane, however, as the acrylic acid content of the copolymer is reduced to 50%, the complexes can be swollen. The water swelling ratios of PEOx–PAA semi-IPNs decrease linearly as the amount of crosslinking agents is increased, and weight loss due to extraction by water shows the same trend as swelling ratio. The T_g values of PEOx–PAA semi-IPNs after extraction by water are several degrees higher than those before extraction. The increment is explained by postulating a rearrangement of PEOx and PAA groups to result in additional hydrogen bonds. Extraction by DMSO removes about 40–50% of the PEOx from the crosslinked network. The incomplete removal is probably a result of topographical constraints against diffusion.

ACKNOWLEDGEMENT

Partial support of this work by Petroleum Research Fund, PRF grant No. 18226-AC7, administered by the American Chemical Society is gratefully acknowledged.

REFERENCES

1 Tsuchida, E. and Abe, K. *Adv. Polym. Sci.* 1982, **45**, 1
2 Bekturov, E. A. and Bimendina, L. A. *Adv. Polym. Sci.* 1982, **41**, 99
3 Lin, P. Y., Clash, C., Aponti, M., Pearce, E. M. and Kwei, T. K. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 603
4 Smith, K. L., Winslow, E. E. and Peterson, D. E. *Ind. Eng. Chem.* 1959, **51**, 1361
5 Tsutsui, T. Nakano, H., Tanaka, R. and Tanaka, T. *Kobunshi Ronbushu* 1978, **35** (8), 517
6 deMaftahi, M. V. and Frechet, J. M. J. *Polymer* 1988, **29**, 477
7 Pearce, E. M., Kwei, T. K. and Min, B. Y. *J. Macromol. Sci.* 1984, **A21**, 1181
8 Fahrenholtz, S. R. and Kwei, T. K. *Macromolecules* 1981, **14**, 1076
9 Pennacchia, J. R., Pearce, E. M., Kwei, T. K., Bulkin, B. J. and Chen, J. P. *Macromolecules* 1986, **19**, 973
10 Min, B. Y. *PhD Dissertation*, Polytechnic Institute of New York, USA, 1984