Study on the morphology and properties of interpenetrating polymer networks of poly(zinc acrylate) and polyacrylonitrile

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A series of semi-interpenetrating polymer networks (IPNs) based on poly(zinc acrylate) and polyacrylonitrile were synthesized by a sequential mode of synthesis. The IPNs were characterized by scanning electron microscopy, i.r. spectroscopy and by measuring crosslink density. Divinyl benzene was used as the crosslinking agent for acrylonitrile, and azobisisobutyronitrile as initiator. Variation in composition of the IPN was achieved by varying the concentration of polymer, monomer, crosslinker, initiator and the viscosity average molecular weight of polymer, and their effects on morphology and crosslinking were examined. The increase in concentration of linear polymer and initiator decreases crosslinking and increases incompatibility, while the increase in concentration of crosslinker increases both crosslinking and phase separation.

(Keywords: poly(zinc acrylate); polyacrylonitrile; IPNs)

INTRODUCTION

Over the past 20 years there has been widespread interest in multicomponent polymer systems, including polyblends, block and graft copolymers and interpenetrating polymer networks (IPNs). Among this diverse group of multicomponent, and in some cases multiphase, polymers, IPNs have perhaps received the most attention, because of their combination of great commercial importance and scientific interest.

The field of IPN study, founded by Millar[1] in 1960, has been advanced mainly by Sperling[2-4] and Frisch[5-7] and their co-workers. While there is much scientific literature concerning IPNs based on polyurethane[8-10], addition polymers[11,12], epoxy resins[13] and phenol formaldehyde resins[14], only a little work has been carried out to date on the use of metal-containing monomer in the synthesis of IPNs. Reza *et al.*[15] have reported the synthesis and morphology of IPNs containing copolymers of acrylamide, methylene bis-acrylamide and vinyl ferrocene. Recently, the synthesis of poly(chromium acrylate)- and acrylonitrile-based IPNs has also been reported[16,17].

Despite the need for a rigorous understanding of the dominant structural parameters determining the overall morphology and properties of such materials, only a few of the cited papers contain an integrated investigation of the effect of structural parameters, such as molecular weight and concentration of the dispersed phase, on phase relationships and other properties of the system. The main goal of this work is therefore to synthesize poly(zinc acrylate)-containing IPN and to find out how the parameters, such as molecular weight and concentration of dispersed phase and crosslinking agent, may determine the morphology and swelling properties of IPNs.

EXPERIMENTAL

Materials

Acrylonitrile was freed from inhibitor by washing with 5% alkali followed by 10% orthophosphoric acid. Next, the monomer was washed well with water, dried over anhydrous calcium chloride and distilled under reduced pressure[18].

Solvents (Qualigens) and divinyl benzene (Merck) were used without further purification.

Azobisisobutyronitrile (AIBN) was recrystallized in methanol (m.p. 102°C).

The zinc acrylate was synthesized by the reported method[19]. Zinc oxide and acrylic acid were taken in stoichiometric ratio and acetone was used as solvent. The reaction mixture was stirred for 22 h. Finally the reaction mixture was filtered to remove any insoluble impurity and solvent acetone was evaportated to obtain zinc acrylate monomer.

Synthesis of poly(zinc acrylate)

Zinc acrylate was polymerized by using styrene arsenic sulfide complex[20] in dimethylsulfoxide (DMSO) as radical initiator at 90 ± 0.1°C for 2 h. Poly(zinc acrylate), with various average molecular weights, was synthesized by using toluene as chain transfer agent.

The intrinsic viscosity (η_{int}) of poly(zinc acrylate) was determined in benzene at 20 ± 0.1°C using an Ubbelohde viscometer.

Synthesis of IPN

The calculated amount of poly(zinc acrylate) was dissolved in benzene and to this 0.5% (w/v) AIBN, 0.1–1.0

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Table 1 Variable manipulation of IPN

Sample no.	[PZnA] (base M) ($\times 10^3$ mol/100 ml)	η_{int}	[AN] (mol/100 ml)	[AIBN] (% w/v)	[DVB] (mol/100 ml)
IPN-1	12.0	0.028	0.30	0.5	0.56
IPN-2	9.0	0.028	0.30	0.5	0.56
IPN-3	6.0	0.028	0.30	0.5	0.56
IPN-4	3.0	0.028	0.30	0.5	0.56
IPN-5	9.0	0.028	0.35	0.5	0.56
IPN-6	9.0	0.028	0.45	0.5	0.56
IPN-7	9.0	0.028	0.60	0.5	0.56
IPN-8	9.0	0.028	0.30	0.5	0.28
IPN-9	9.0	0.028	0.30	0.5	0.84
IPN-10	9.0	0.028	0.30	0.5	0.98
IPN-11	9.0	0.028	0.30	0.3	0.56
IPN-12	9.0	0.028	0.30	0.1	0.56
IPN-13	9.0	0.032	0.30	0.5	0.56
IPN-14	9.0	0.037	0.30	0.5	0.56
IPN-15	9.0	0.042	0.30	0.5	0.56

mol/100 ml of divinyl benzene and 0.15–0.60 mol/100 ml of acrylonitrile were added and polymerized for 2.5 h at 60°C under a blanket of nitrogen. Finally, the IPN was vacuum dried until a constant weight was obtained. A series of 15 IPNs was prepared with the variables shown in *Table 1*. The principal chemical variable included a systematic variation of concentration of poly(zinc acrylate) (PZnA), acrylonitrile (AN), divinyl benzene (DVB) and AIBN.

Characterization of IPN

The crosslink density of a polymer network is controlled primarily by the amount of chemical crosslinking agent added or the method of crosslinking. However, branching reaction, chain transfer and termination introduces considerable uncertainty as to the exact crosslink density. Depending upon the reaction conditions, some portion of polymer may not be effectively incorporated in network characterization.

The two parameters generally employed in network characterization, namely M_c (the average molecular weight of polymer between crosslinks) and the percentage of extractable material removed while approaching equilibrium swelling, have been studied.

Swelling properties

Before proceeding to the measurement of swelling of polymer networks in different solvents, the soluble or uncrosslinked component of IPN was removed with the help of a Soxhlet extractor. The percentage extractable material was calculated as follows:

$$\%\ \text{extractable material} = \frac{W_b - W_a}{W_b} \times 100$$

where W_b = weight of IPN before extraction and W_a = weight of IPN after extraction.

Swelling measurements were made by soaking the sample in solvents (dimethylformamide (DMF), dioxane, DMSO, benzene, toluene) until an equilibrium weight was achieved ($\sim$24 h). Weight measurements were made by blotting the samples dry and immediately weighing them. The swelling solvent was then removed by heating the samples to 60°C under vacuum until equilibrium weight was achieved. The percentage swelling values reported were determined from the equilibrium swollen weight and the final equivalent dried weight to account for solvent extraction of low molecular weight components. The relationship used to calculate percentage swelling is as follows[21]:

$$\%\ \text{swelling} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s = weight of swollen IPN and W_d = weight of dried IPN.

The crosslink density of the network was determined by using swelling data of IPN in dioxane with the help of the Flory–Rehner equation[22,23]:

$$\frac{1}{M_c} = -\frac{\ln(1 - V_p) + V_p + X_{12}V_p^2}{\rho V_1 (V_p^{1/3} - \frac{1}{2}V_p)}$$

where M_c = average molecular weight of network between crosslinks, ρ = density of network, V_1 = molar volume of solvent, V_p = volume fraction of polymer in swollen gel, X_{12} = polymer–solvent interaction parameter, calculated as 0.342 by the following expression[23]:

$$X_{12} = B + \frac{V_1}{RT}(\delta_p - \delta_s)^2$$

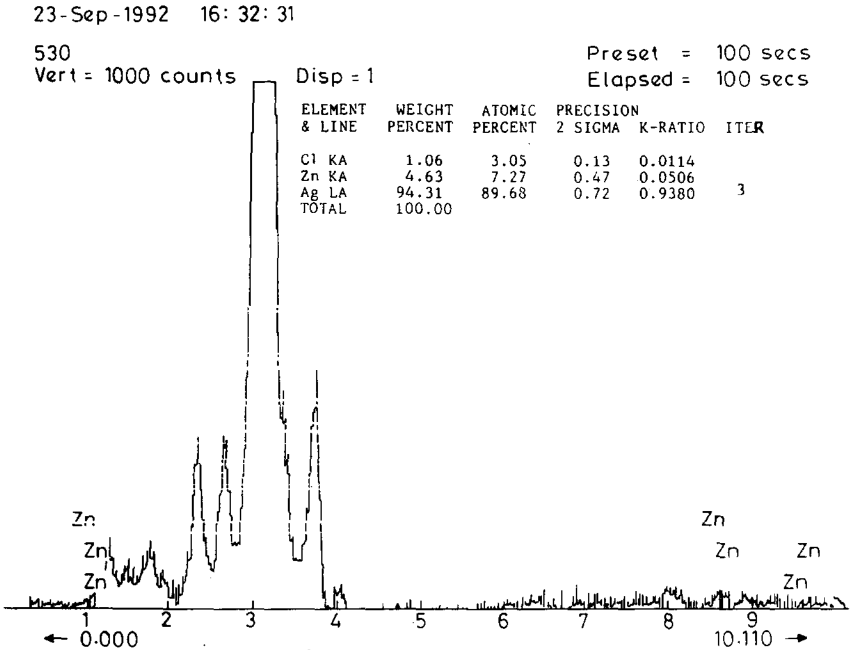
where δ_p and δ_s are the solubility parameters of polymer and swelling solvent, respectively, and B = the lattice constant, the value of which is taken as 0.34 (ref. 23).

Morphology

The morphology of the IPNs thus prepared was studied by scanning electron microscopy (SEM). Samples were mounted on a SEM stub by silver adhesive paste and coated with silver in an SEM coating unit. The samples were then scanned in a Jeol JSM 840A scanning electron microscope.

Thermal properties

The glass transition temperature was measured with a differential scanning calorimeter (General V4.1C Dupont



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ELEMENT   WEIGHT   ATOMIC   PRECISION
& LINE    PERCENT  PERCENT  2 SIGMA  K-RATIO   ITER

Cl KA       1.06     3.05    0.13    0.0114
Zn KA       4.63     7.27    0.47    0.0506
Ag LA      94.31    89.68    0.72    0.9380      3
TOTAL     100.00
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Figure 1 Spot analysis curve of IPN-2 (range = 10.230 keV)

Table 2 Percentage swelling of IPN in different solvents, percentage extractable material and metal content (determined by SEM)

Sample no.	Solvents					Extractable material (%)	Metal content (%)
	DMF	Dioxane	DMSO	Benzene	Toluene		
IPN-1	301.3	343.04	289.30	128.70	171.40	32.05	1.06
IPN-2	205.50	183.80	134.40	91.20	104.90	35.81	7.27
IPN-3	180.44	171.70	122.30	76.12	87.90	31.52	–
IPN-4	56.12	49.62	39.47	14.72	27.40	18.54	15.49
IPN-5	211.65	190.60	143.50	72.40	203.90	13.51	–
IPN-6	202.50	171.03	119.50	84.30	88.50	23.58	12.89
IPN-7	113.18	162.82	99.90	51.46	65.86	26.38	20.83
IPN-8	289.90	257.67	235.50	117.56	155.80	86.86	0.98
IPN-9	145.88	137.03	127.02	89.25	100.14	19.32	26.62
IPN-10	93.82	36.04	33.44	32.15	33.73	12.50	–
IPN-11	96.81	74.84	85.11	70.01	72.48	31.68	8.97
IPN-12	71.97	66.40	65.10	51.05	52.82	30.28	–
IPN-13	195.32	146.76	133.51	81.48	91.71	25.64	–
IPN-14	135.32	94.66	128.01	75.31	85.31	26.21	6.10
IPN-15	90.03	79.27	96.20	54.73	76.25	11.33	5.41

model 2000). D.s.c. curves were recorded under nitrogen atmosphere at a flow rate of 10°C min^{-1}. The sample weight was 5.0 ± 0.1 mg.

RESULTS AND DISCUSSION

Qualitative analysis of nitrogen and zinc confirmed the incorporation of both components in the network. Further, nitrogen was confirmed by i.r. spectra ($-\mathrm{C{\equiv}N}$ group, 2260 cm^{-1}) and zinc by spot analysis provided by SEM (*Figure 1*).

Emphasis is given to the effect of [PZnA], [AN], [DVB], [AIBN], swelling, average molecular weight between crosslinks (M_c) and phase behaviour.

The results of swelling in various solvents and the extraction study employing DMF and the percentage of metal (determined by SEM) are summarized in *Table 2*. The low percentage of extractable material shown in the table may be due to sufficient crosslinking of the polymer making them insoluble. To some extent, grafting of linear polymer to the other crosslinked polymer could also be the reason for the above result. Almost all the samples show swelling, therefore M_c is an inverse function of the percentage of metal in the sample, i.e. increased metal content increases crosslinking or *vice versa*.

Effect of [*crosslinker*]

Table 3 shows that as [DVB] is increased, the percentage yield increases, as expected. The reason for this may be that increased crosslinking agent increases crosslinking and consequently the percentage yield. The percentage swelling of IPN in different solvents and M_c are inverse functions of [DVB] (*Tables 2* and *3*). The explanation is that increased [DVB] increases the crosslinking level which results in decreased swelling and M_c.

Table 3 Effect of [DVB] on IPN properties. [PZnA] (base M) = 9.0×10^{-3} mol/100 ml; [AN] = 0.30 mol/100 ml; [AIBN] = 0.5% (w/v)

[DVB] (mol/100 ml)	Yield (%)	Swelling in DMF (%)	Density (g cm^{-3})	M_c (g mol^{-1})
0.28	6.53	298.90	0.982	2522.98
0.56	23.05	205.50	0.979	1312.35
0.84	39.96	145.88	0.934	650.46
0.98	30.70	43.82	0.937	119.64

Table 4 Effect of [PZnA] (base M) on IPN properties. [AN] = 0.30 mol/100 ml; [DVB] = 0.56 mol/100 ml; [AIBN] = 0.50% (w/v)

[PZnA] (base M) ($\times 10^3$ mol/100 ml)	Yield (%)	Swelling in DMF (%)	Density (g cm^{-3})	M_c (g mol^{-1})
12.0	22.70	301.30	0.968	2463.55
9.0	23.05	205.50	0.979	1312.35
6.0	25.01	180.44	0.982	1064.34
3.0	25.23	56.12	0.994	186.14

Table 5 Effect of [AN] on IPN properties. [PZnA] (base M) = 9.0×10^{-3} mol/100 ml; [DVB] = 0.56 mol/100 ml; [AIBN] = 0.5% (w/v)

[AN] (mol/100 ml)	Yield (%)	Swelling in DMF (%)	Density (g cm^{-3})	M_c (g mol^{-1})
0.15	31.17	211.65	0.967	1337.61
0.30	23.05	205.50	0.798	1312.35
0.45	18.10	202.50	0.982	1296.01
0.60	19.40	113.81	0.966	477.51

Effect of composition

The effect of composition on IPN properties, i.e. swelling and crosslink density, follows a logical trend since an increase in PZnA content results in increased swelling and M_c (*Table 4*). This implies that the presence of PZnA restricts crosslinking of polyacrylonitrile (PAN) network. This restriction is due to an overall decrease in concentration of crosslinking sites of AN with increased PZnA. Furthermore, in solution graft copolymerization it is generally believed[24] that polymer becomes grafted and crosslinked to some extent during reaction of monomer. As the PZnA content increases the probability of grafting by AN also increases, which may subsequently produce some degree of crosslinking in PZnA. Consequently, it suppresses the crosslinking of AN to some extent. A similar explanation can be given for the observation that the percentage swelling and M_c are inverse functions of [AN] (*Table 5*).

Effect of viscosity average molecular weight, $\bar{M}_v$, of poly(zinc acrylate)

The effect of $\bar{M}_v$ was studied. There was a clear increase in swelling and therefore in M_c with decreased $\bar{M}_v$ of PZnA. The conclusion is that a large dimension of linear polymer facilitates crosslinking. This phenomenon can be attributed to decreased molecular mobility of polymer chain with increased molecular weight, consequently facilitating grafting of linear polymer to crosslinked polymer. This explanation is supported by the finding that the percentage of extractable material or the uncrosslinked polymer decreases with increase of η_{int} (*Tables 2* and *6*).

Effect of [initiator]

Table 7 presents data on the effect of [AIBN] on swelling and M_c of IPN. The data show that both swelling and M_c increase with increase of [AIBN].

Morphology

SEM observations reveal that the specimens have a mottled texture; there are two distinct phase domains owing to phase separation of the two component networks. PZnA is the continuous phase in which the second component, PAN, is entangled. In general, all SEM photographs of semi-IPNs show the complex structure and reveal the internal appearance of a sponge with submicroscopic porosity. The phase separation in the IPN is supported by the d.s.c. curve of IPN-2 (*Figure 2*), which shows two T_g values at 174 and 220°C.

White dots in *Figure 3* show the positions of metal atoms in *Figure 1*. The white clusters in *Figure 4* represent the PAN network and the dark continuous phase is due to PZnA. It is evident that the morphology depends on the composition as illustrated: decreased $\bar{M}_v$ of PAN

Table 6 Effect of intrinsic viscosity (η_{int}) of PZnA (in benzene at 20±0.1°C) on IPN properties. [PZnA] (base M) = 9.0×10^{-3} mol/100 ml; [AN] = 0.30 mol/100 ml; [DVB] = 0.56 mol/100 ml; [AIBN] = 0.5% (w/v)

η_{int}	Yield (%)	Swelling in DMF (%)	Density (g cm^{-3})	M_c (g mol^{-1})
0.028	23.05	205.50	0.979	1312.35
0.032	21.47	191.32	0.978	1159.31
0.037	23.62	135.32	0.963	627.53
0.042	20.08	90.03	0.958	330.52

Table 7 Effect of [AIBN] on IPN properties. [PZnA] (base M) = 9.0×10^{-3} mol/100 ml; [AN] = 0.30 mol/100 ml

[AIBN]	Yield (%)	Swelling in DMF (%)	Density (g cm^{-3})	M_c (g mol^{-1})
0.1	24.44	81.97	0.957	238.15
0.3	27.53	96.81	9.948	357.74
0.5	23.05	205.50	0.979	1312.35

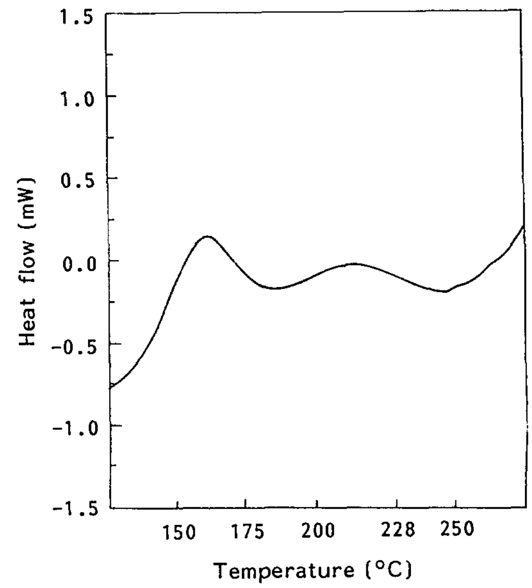

Figure 2 D.s.c. curve of IPN-2

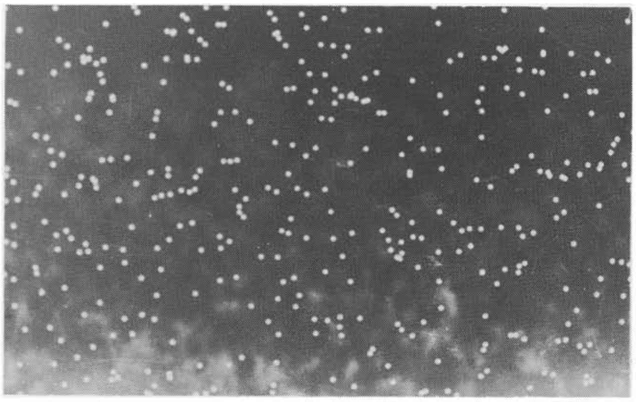

Figure 3 SEM photograph showing positions of metal atoms in *Figure 4* (by X-ray analysis)

Figure 4 SEM photograph of IPN-15 (magnification 1500 ×)

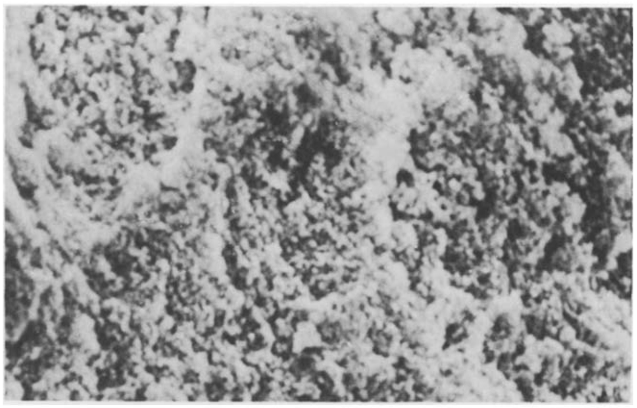

Figure 5 SEM photograph of IPN-2 (magnification 1500 ×)

increases phase mixing of IPN-15 and IPN-2 at a magnification of 1500 ×. IPN-15 shows clear phase separation (*Figure 4*), whereas IPN-2 shows partial phase separation (*Figure 5*). IPN-1 ([PZnA] base $M = 12 \times 10^{-3}$ mol/100 ml) (*Figure 6*) shows a clear phase separation which is decreased in IPN-2 (*Figure 5*) ([PZnA] base $M = 9.0 \times 10^{-3}$ mol/100 ml). The conclusion is that a decrease in linear polymer content increases compatibility. The SEM study reveals that phase separation is intensified with increase of [crosslinker] and [initiator] (figures not shown here).

CONCLUSION

The major conclusions drawn are as follows. Crosslinking is a function of [crosslinker] and an inverse function of

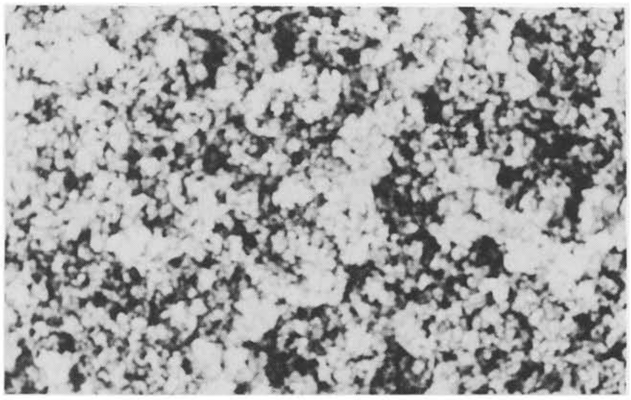

Figure 6 SEM photograph of IPN-1 (magnification 1500 ×)

M_c, [linear polymer], [initiator] and $\bar{M}_v$ of the linear polymer. Phase separation is a function of [linear polymer], [crosslinker] and [initiator], and an inverse function of $\bar{M}_v$ of the linear polymer.

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REFERENCES

1 Millar, J. R. *J. Chem. Soc.* 1960, 311

2 Donatelli, A. A., Sperling, L. H. and Thomas, D. A. *Macromolecules* 1976, **9**, 671

3 Sperling, L. H. and Carraher, C. E. *Polym. Mater. Sci. Eng.* 1990, **62**, 222

4 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum, New York, 1981

5 Frisch, H. L., Klempner, D., Yoon, H. K. and Frisch, K. C. *Macromolecules* 1980, **13**, 1016

6 Frisch, H. L., Gebreyes, K. and Frisch, K. C. *J. Polym. Sci.: Part A; Polym. Chem.* 1988, **26**, 2589, 3391

7 Klempner, D. and Frisch, H. L. 'Polymer Alloys II', Plenum, New York, 1980

8 Dzomo, H., Morin, A., Damyanidu, M. and Meyer, G. *Polymer* 1983, **24**, 65

9 Patel, P. and Suther, B. *Polymer* 1991, **31**, 339

10 Natchimuthu, N., Rajalingam, P. and Radhakrishnan, G. *J. Appl. Polym. Sci.* 1990, **41**, 3059

11 Mathew, A. and Deb, P. C. *J. Appl. Polym. Sci.* 1992, **45**(12), 2145

12 Yeo, J. K., Sperling, L. H. and Thomas, D. A. *Polym. Eng. Sci.* 1982, **22**(3), 178

13 Fukami, A., Tisaka, K. and Etoh, S. *J. Makromol. Sci. Phys. B* 1989, **28**(2), 249

14 Yang, T. P., Kwei, T. K. and Pearce, E. M. *J. Appl. Polym. Sci.* 1990, **41**, 1327

15 Reza, A., Benedetto, C., Lora, S., Palma, G., Russo, U., Sam, F. and Zeeca, M. *Adv. Mater.* 1990, **2**(9), 412

16 Gupta, N. and Srivastava, A. K. *High Perform. Polym.* 1992, **4**(4), 225

17 Gupta, N. and Srivastava, A. K. *Macromol. Rep. A* 1993, **30** (Suppl. 5), 375

18 Jijie, K., Santappa, M. and Mahadevan, V. *J. Polym. Sci., Polym. Chem. Edn* 1966, **4**, 393

19 Gronowski, A. and Woztezak, Z. *J. Therm. Anal.* 1983, **26**, 233

20 Shukla, P. and Srivastava, A. K. *Makromol. Chem. Rapid Commun.* 1989, **10**, 589

21 Chatterji, P. R. *J. Appl. Polym. Sci.* 1989, **37**, 2203

22 Collins, E. A., Bares, J. and Billmeyer, F. W. Jr 'Experiments in Polymer Science', Wiley, New York, 1973

23 Xiew, H., Ping, Z. H., Xie, J. W. and Yu, T. Y. *J. Polym. Sci. Part A: Polym. Chem.* 1990, **28**, 585

24 Malen, G. E. and Keskkula, H. *J. Polym. Sci. Part A-1* 1982, **4**, 1595