Interpenetrating Polymer Networks (IPNs) from Poly(metal acrylates): Synthesis and Properties

Nidhi Gupta and A. K. Srivastava*

Department of Chemistry, H. B. Technological Institute, Kanpur-2, India

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ABSTRACT: A series of semi-interpenetrating polymer networks (semi-IPNs) based on acrylonitrile and poly(metal acrylates) of chromium, zinc, and copper were prepared. They are formed by cross-linking the acrylonitrile (monomer II) with divinylbenzene in the presence of linear poly(metal acrylate) (Polymer I). Investigations were carried out by swelling measurements, IR spectroscopy, differential scanning calorimetry, thermal analysis, and scanning electron microscopy. It was concluded that the swelling and, therefore, M_c follow the order Zn-IPN > Cr-IPN > Cu-IPN. The thermal stability of the various IPNs at 200, 300, and 400 °C have the following order: Cu-IPN > Cr-IPN > Zn-IPN. The T_g values have also been determined for the IPN samples.

Introduction

The chemical and physical combination methods and properties of multipolymers have been of commercial and academic interest, since they provide a convenient route for the modification of properties to meet specific needs. Among these methods, considerable interest has been given to IPNs.

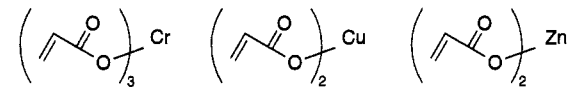
IPNs are widely used in various modern technologies. Presently, they are one of the most promising and important categories of polymers with properties which can be quite different from their component networks. These complex systems are capable of realizing a wide spectrum of physico-chemical properties which depend on the extent of component compatibility.

Although several papers about IPNs have been published, most of them describe studies of IPNs from polyurethane,[1-3] epoxy,[4] phenol–formaldehyde resins,[5] and some conventional vinyl polymers.[6,7] Studies on IPNs from metal containing monomers have started only recently. In 1990 Reza et al.[8] reported the synthesis and morphology of IPN containing copolymers of acrylamide, methylenebis(acrylamide), and vinyl ferrocene. Recently, synthesis and properties of chromium and zinc acrylate based IPNs have also been reported[9-11] for the first time from this laboratory. The IPNs[9-11] showed better thermal properties as compared to other IPNs containing acrylonitrile.[12]

This inspired us to extend our studies to the IPNs from other metal acrylates such as poly(copper acrylate). The present article details the synthesis and properties of IPN containing poly(copper acrylate) and acrylonitrile as polymer 1 and monomer 2, respectively, and a comparative account of IPNs from copper, zinc, and chromium acrylate.

Experimental Section

Materials. Acrylonitrile was purified by the standard method.[13] Solvents (Qualigens) and divinylbenzene (Merck) were used without further purification. AIBN was recrystallized in methanol (mp, 102 °C). The copper, zinc,[14] and chromium[15] acrylates were synthesized by the reported methods. The metal oxides were stirred for 22 h with a stoichiometric amount of acrylic acid using acetone as the solvent. The structures of various metal acrylates are as follows:

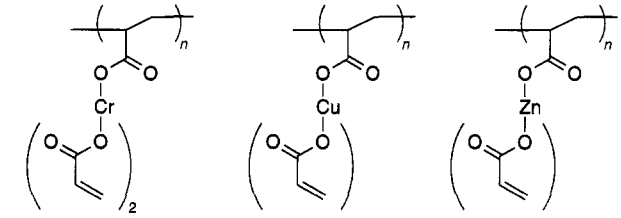


chromium acrylate copper acrylate zinc acrylate

Synthesis of Poly(metal acrylates). Copper acrylate was polymerized by using the styrene–arsenic sulfide complex[16] in DMF as the radical initiator at 90 ± 1.0 °C for 12 h. Poly(copper acrylates) of various average molecular weights were synthesized by using toluene as the chain transfer agent.

Chromium acrylate was polymerized by using the styrene–arsenic sulfide complex in DMF as the radical initiator at 90 ± 1.0 °C for 5 h.

Zinc acrylate was polymerized by using the styrene–As_2S_3 complex in DMSO as the radical initiator at 90 ± 1.0 °C for 2 h. The structures of various poly(metal acrylates) are as follows:



poly(chromium acrylate) poly(copper acrylate) poly(zinc acrylate)

Synthesis of IPN. The calculated amount of poly(copper acrylate) was dissolved in benzene, and to this were added 0.5% (w/v) AIBN, 0.5–0.2 mol/100 mL divinylbenzene, and 0.15–0.60 mol/10 mL acrylonitrile. The mixture was polymerized for 3 h at 60 °C under a blanket of nitrogen. Finally, the IPN was vacuum dried until a constant weight was obtained. A series of 12 IPNs were prepared with the variables manipulated in Table 1. The principal chemical variable includes a systematic variation of concentration of poly(copper acrylate), acrylonitrile, divinylbenzene, and AIBN.

IPNs with poly(chromium acrylate)[10] and poly(zinc acrylate)[11] were also synthesized by a similar method.

Characterization. (a) Polymer Characterization. For polymer characterization infrared spectroscopic analysis was performed on a Perkin-Elmer IR spectrophotometer. The presence of an easily descernible band at 1600–1700 cm^{-1} due to the carbonyl group is characteristic of a metal acrylate (Figure 1). The intrinsic viscosity (η_{int}) of poly(copper acrylate) was determined in benzene at 30 ± 1.0 °C using an Ubbelhode viscometer.

(b) Network Characterization. The cross-linked density of the polymer network is primarily controlled by the amount of chemical cross-linking agent added or the method of cross-

* To whom correspondence should be addressed.

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Table 1. Variable Manipulation in IPN

sample no.	10^{-3}[PCuA] (base M), mol/100 mL	η_{int} of PCuA	[AN], mol/100 mL	[AIBN], w/v	[DVB], mol/100 mL
IPN-1	9.0	0.043	0.30	0.5	0.112
IPN-2	6.0	0.043	0.30	0.5	0.112
IPN-3	3.0	0.043	0.30	0.5	0.112
IPN-4	9.0	0.043	0.15	0.5	0.112
IPN-5	9.0	0.043	0.45	0.5	0.112
IPN-6	9.0	0.043	0.60	0.5	0.112
IPN-7	9.0	0.043	0.30	0.5	0.056
IPN-8	9.0	0.043	0.30	0.5	0.196
IPN-10	9.0	0.043	0.30	0.30	0.0112
IPN-11	9.0	0.033	0.30	0.5	0.112
IPN-12	9.0	0.021	0.30	0.5	0.112
IPN-13	9.0	0.014	0.30	0.5	0.112

linking. However, branching reaction, chain transfer, and termination introduce considerable uncertainty as to the exact crosslinked density. Depending upon the reaction conditions, some portion of the polymer may not be effectively incorporated in network characterization.

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

Swelling Property. (I) Swelling measurements were made by soaking the samples in solvents (DMF, dioxane, DMSO, benzene, and toluene) until an equilibrium weight was achieved (approximately 24 h). Weight measurements were made by blotting the samples dry and immediately weighting them. The swelling solvent was then removed by heating the samples to 60 °C under vacuum until the equilibrium weight was achieved. The reported swelling percentages were determined from the equilibrium swollen weight and the final dried weight to account for solvent extraction of low molecular weight components. The relationship used to calculate percentage swelling is as follows[17]

$$\% \text{ swelling} = \frac{w_s - w_d}{w_d} \times 100$$

where w_s is the weight of swollen IPN and w_d is the weight of dried IPN.

(II) The cross-linked density of the network was determined by using the swelling data of the IPN in DMF with the help of the Flory–Rehner equation[18–20]

$$\frac{1}{M_c} = \frac{-\ln(1 - v_p) + v_p + x_{12}v_p^2}{\varrho v_1(v_p^{1/3} - v_p/2)}$$

where M_c is the average molecular weight of network between cross-links, ϱ is the density of the network, v_1 is the molar volume of the solvent, v_p is the volume fraction of polymer in the swollen gel, and x_{12} is the polymer solvent interaction parameter calculated by the following expression[20]

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

where δ_p and δ_s are solubility parameters of the polymer and swelling solvent, respectively, and B is the lattice constant, the value of which is taken as 0.34.[20]

IR Spectroscopy. IR spectra of the IPNs were recorded on a Perkin-Elmer IR spectrophotometer.

Differential Scanning Calorimetry (DSC). DSC curves were recorded on a general V2-2A DuPont 9900 differential scanning calorimeter under a nitrogen atmosphere at a heating rate of 10 °C/min. The sample weights were 5.0 ± 0.1 mg.

Thermal Stability. The thermal stability was determined by thermogravimetric analysis (TGA) performed on a TG-750 thermogravimetric analyzer (Stanton Redcraft, U.K.).

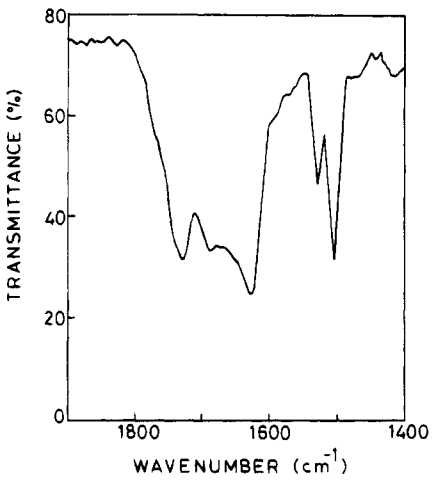

Figure 1. IR spectrum of poly(copper acrylate).

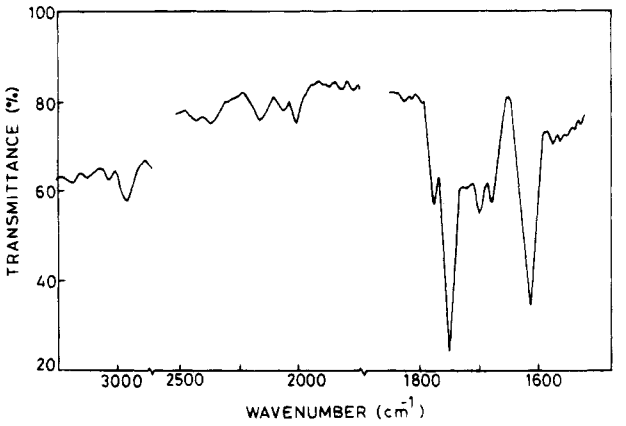

Figure 2. IR spectrum of IPN.

Morphology. The morphology of the IPNs thus prepared was studied by using a scanning electron microscope. Samples were mounted on a SEM stub by silver adhesive paste, coated with silver in SEM coating equipment, and scanned in a JEOL JSM 840A scanning electron microscope.

Results and Discussion

Structural evidence for the IPN from poly(copper acrylate) comes from the IR spectrum (Figure 2), indicating the characteristic frequency of a cyanide group (—C≡N) at 2260 cm^{-1} and a carboxylate group (—C(O)=O) around 1600–1700 cm^{-1}. A sharp intense and easily discernible band around 3000 cm^{-1} may be assigned to the aromatic ring of divinylbenzene. Nitrogen and copper were confirmed by qualitative analysis.

Further nitrogen was confirmed by IR spectra (—C≡N group, 2260 cm^{-1}), and copper, by spot analysis of IPN samples by SEM (Figure 3). The ratio of the cyanide and carboxylate peaks from the IR spectra is 0.25:1, while from the original monomer II/polymer I feed ratio it is 16.6:1. This lowering of the cyanide fraction shows the possibility that few of the cyanide groups are involved in some type of bonding, i.e., they are not free.[21] The bonding may be due to complex formation between —C≡N (lone pair of nitrogen) and Cu (transition metal). From this observation it is concluded that some extent of grafting occurs in the IPN system; i.e. the present IPN (Cu-IPN) is a type of grafted semi-IPN. Grafting was further confirmed by a positive qualitative test for copper in IPN after its Soxhlet extraction with DMF.

An emphasis is given to the effects of [PCuA], [AN], [DVB], [AIBN], and η_{int} of PCuA on properties such as

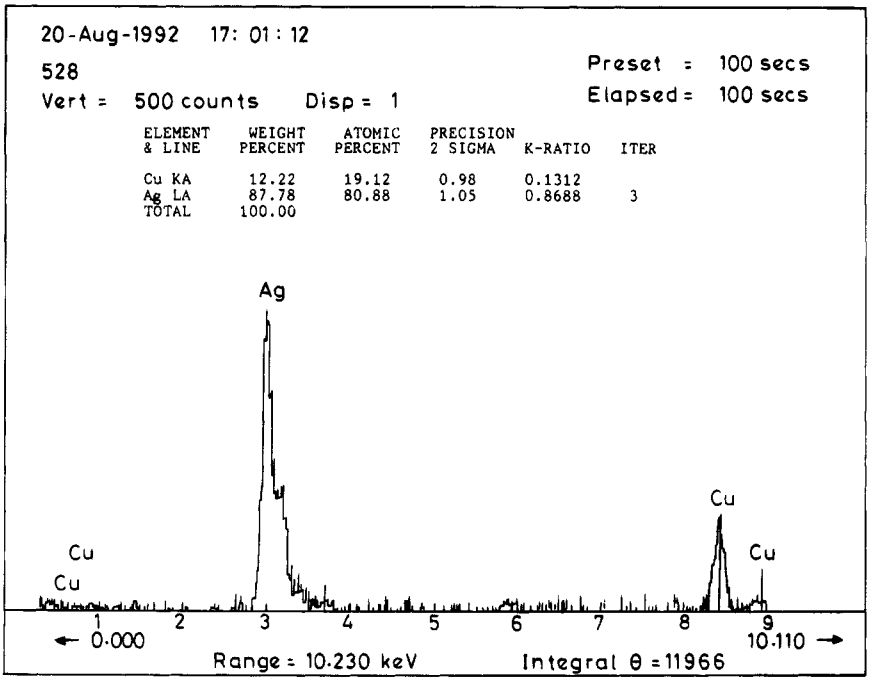

Figure 3. Results of spot analysis of IPN by SEM.

Table 2. Percentage Swelling of IPN in Different Solvents and Percentage of Extractable Material

	% swelling in solvents					% extractable
sample	DMF	DMSO	dioxane	benzene	toluene	material
IPN-1	30.73	34.6	18.81	15.74	18.18	14.97
IPN-2	43.69	58.30	29.8	24.58	23.67	14.21
IPN-3	64.2	69.65	50.3	34.10	34.45	14.16
IPN-4	35.6	34.35	20.89	18.77	19.06	18.8
IPN-5	25.54	30.10	17.96	14.8	17.6	12.51
IPN-6	39.6	47.63	17.96	14.8	17.6	12.51
IPN-7	40.1	54.52	30.71	18.25	34.6	10.8
IPN-8	24.4	36.95	18.8	12.02	15.5	17.4
IPN-10	16.76	28.8	16.76	11.05	14.9	22.56
IPN-11	62.37	75.36	51.19	31.08	35.67	16.09
IPN-12	69.92	89.84	59.36	40.01	44.18	19.98
IPN-13	79.57	95.40	64.17	51.75	56.2	22.96

Table 3. Effect of Concentration of Divinylbenzene on IPN Properties[a]

[DVB], mol/100 mL	% yield	% swelling in DMF	density, g/cm^3	M_c, g/mol
0.056	20.19	40.1	1.098	153.15
0.112	21.47	30.73	1.1033	113.26
0.196	23.19	24.4	1.0978	87.76

[a] [PCuA] (base M) = 9.0 × 10^{-3} mol/100 mL, [AN] = 0.30 mol/100 mL, [AIBN] = 0.5% (w/v).

swelling, average molecular weight between cross-links (M_c), and phase behavior.

The results of swelling in various solvents and extraction studies employing DMF are summarized in Table 2. The low percentage of extractable material shown in the table may be due to proper and sufficient cross-linking of polymers making them insoluble. To some extent, grafting of a linear polymer to the other cross-linked polymer can also be the reason for the above results.

(1) Effect of the Concentration of Cross-Linking Agent. Table 3 shows as [DVB] is increased, the percentage yield of IPN increases, as expected. The reason for this observation may be that increased [cross-linking agent] increases cross-linking and consequently the percentage yield. The percentage swelling of IPN

Table 4. Effect of [Acrylonitrile] on IPN Properties[a]

[AN], mol/100 mL	% yield of IPN	% swelling in DMF	density, g/cm^3	M_c, g/mol
0.15	29.25	35.6	1.1031	133.58
0.30	21.47	30.73	1.1033	113.26
0.45	16.68	25.54	1.1098	93.55
0.60	16.75	39.6	1.1130	155.24

[a] [PCuA] (base M) = 9.0 × 10^{-3} mol/100 mL, [DVB] = 0.112 mol/100 mL, [AIBN] = 0.5% (w/v).

Table 5. Effect of [PCuA] (Base M) on IPN Properties[a]

10^{-3}[PCuA] (base M), mol/100 mL	% yield of IPN	% swelling in DMF	density, g/cm^3	M_c, g/mol
9.0	21.47	30.73	1.1033	113.26
6.0	25.23	43.69	1.086	165.86
3.0	26.58	64.2	1.082	275.51

[a] [DVB] = 0.112 mol/100 mL, [AN] = 0.30 mol/100 mL, [AIBN] = 0.5% (w/v).

in different solvents and M_c are inverse functions of [DVB] (Tables 2 and 3). The explanation is that the increase of [DVB] increases the cross-linking level which results in a decrease of swelling and M_c.

(2) Effect of Composition. The effect of composition on IPN properties, i.e. swelling and cross-linked density, follows a logical trend since an increase in [acrylonitrile] decreases swelling and M_c (Tables 2 and 4). This is due to an overall increase in concentration of cross-linking sites of AN with increased [AN]. However, after a certain limit swelling and M_c start increasing. Furthermore, an increase in PCuA component decreases swelling and M_c (Tables 2 and 5). The explanation is that in solution graft copolymerization it is generally believed that polymer I becomes grafted and cross-linked to some extent during the reaction of monomer II.[22] As [PCuA] increases, the probability of grafting by acrylonitrile also increases which may subsequently produce some degree of cross-linking of acrylonitrile. The grafting reaction is further confirmed by the qualitative analysis of IPN after Soxhlet extraction with DMF, showing a positive test for copper.

Table 6. Effect of [AIBN] on IPN Properties[a]

% [AIBN] (w/v)	% yield of IPN	% swelling in DMF	density, g/cm^3	M_c, g/mol
0.5	21.47	30.73	1.1033	113.26
0.3	10.72	24.2	1.1058	87.88

[a] [PCuA] (base M) = 9.0×10^{-3} mol/100 mL, [AN] = 0.3 mol/100 mL, [DVB] = 0.112 mol/100 mL.

Table 7. Effect of η_{int} of PCuA on IPN Properties[a]

η_{int}	% yield of IPN	% swelling in DMF	density, g/cm^3	M_c, g/mol
0.043	21.47	30.73	1.1033	113.26
0.033	47.61	62.37	1.0649	254.31
0.021	60.22	69.92	1.062	296.39
0.014	67.61	79.57	1.0965	307.24

[a] [PCuA] (base M) = 9.0×10^{-3} mol/100 mL, [AN] = 0.3 mol/100 mL, [DVB] = 0.112 mol/100 mL, [AIBN] = 0.5% (w/v).

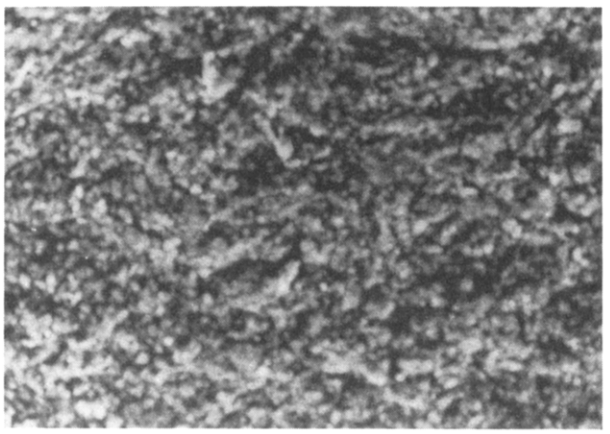

Figure 4. SEM photograph of IPN-1 at a magnification of 1500 times (reduced to 80% for publication).

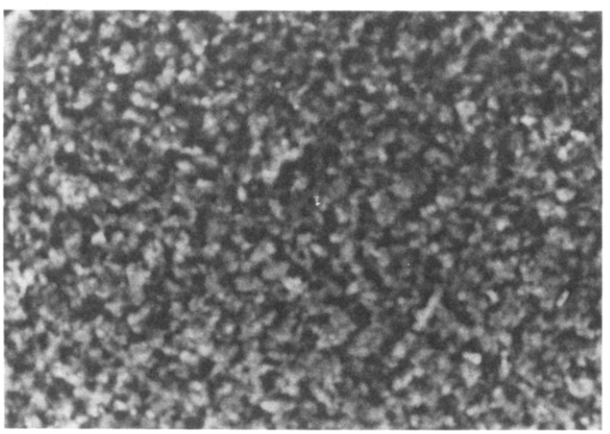

Figure 5. SEM photograph of IPN-11 at a magnification of 1500 times (reduced to 80% for publication).

(3) Effect of the Initiator Concentration. Tables 2 and 6 explore that both swelling and M_c of IPN increase with an increase of [AIBN].

(4) Effect of η_{int} of PCuA. The effect of the average molecular weight of PCuA has also been studied, and results are depicted in Tables 2 and 7. A clear increase in swelling and therefore M_c with a decrease of η_{int} of PCuA is seen; the conclusion is that the large size of the linear polymer facilitates cross-linking. This phenomenon is attributed to a decrease of molecular mobility of the polymer chain with an increased molecular weight, consequently facilitating grafting of the linear polymer to the cross-linked polymer. This explanation is supported by the results that the percent extractable material or the uncross-linked polymer decreased with an increase of η_{int} (Table 2).

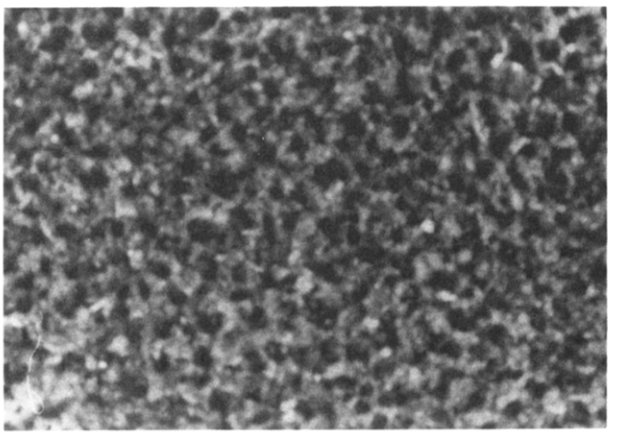

Figure 6. SEM photograph of IPN-13 at a magnification of 1500 times (reduced to 80% for publication).

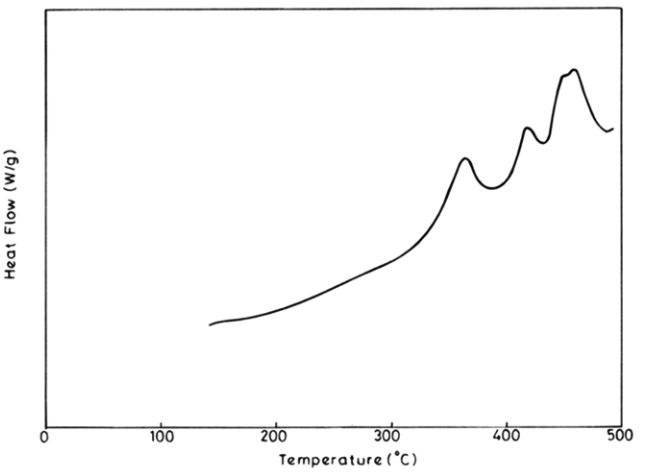

Figure 7. DSC curve of IPN with copper acrylate (Cu-IPN).

Table 8. Effect of Different Metal Acrylates on IPN Properties[a]

sample[b]	% yield of IPN	% swelling in DMF	% extractable material	density, g/cm^3	M_c, g/mol
Cr-IPN	29.3	82.3	23.95	1.0027	325.56
Zn-IPN	23.05	205.5	32.05	0.979	1312.35
Cu-IPN	21.47	30.73	14.87	1.1033	113.26

[a] [poly(metal acrylate)] (base M) = 9.0×10^{-3} mol/100 mL, [AN] = 0.3 mol/100 mL, [DVB] = 0.112 mol/100 mL, [AIBN] = 0.5% (w/v). [b] Poly(metal acrylates): Cr-IPN = PCrA, Zn-IPN = PZnA, Cu-IPN = PCuA.

Table 9. Thermal Stability and Glass Transition Temperature (T_g) of IPNs

sample	% weight at temp 200 °C	300 °C	400 °C	glass transition temp (T_g), °C
Cr-IPN	97.0	84.0	80.0	81.2, 150
Cu-IPN	98.0	93.0	89.0	349.8, 412.2
Zn-IPN	93.0	78.0	70.0	174, 228

Morphology and Glass Transition Behavior. The scanning electron microscope is an excellent tool for the examination of surface morphology. The semi-IPNs prepared for this study contained poly(copper acrylate) of different viscosity average molecular weights ($\bar{M}_v$), IPNs can exhibit a characteristic cellular morphology where the first uncrosslinked component poly(copper acrylate) constitutes the continuous phase.[23] The second component acrylonitrile is entangled in the matrix of PCuA. In general, all SEM photographs of semi-IPNs

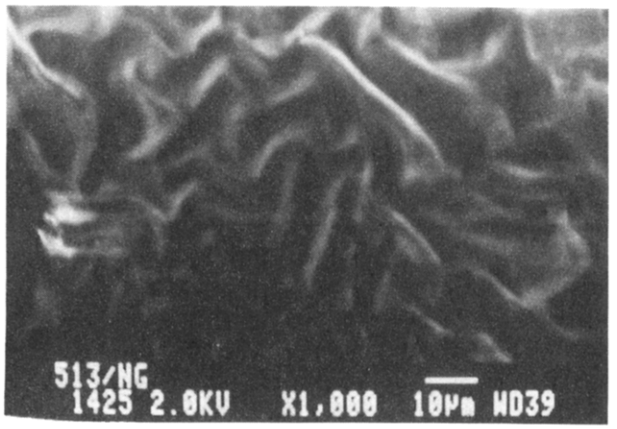

Figure 8. SEM photograph of IPN with PCrA at a magnification of 1000 times (reduced to 80% for publication).

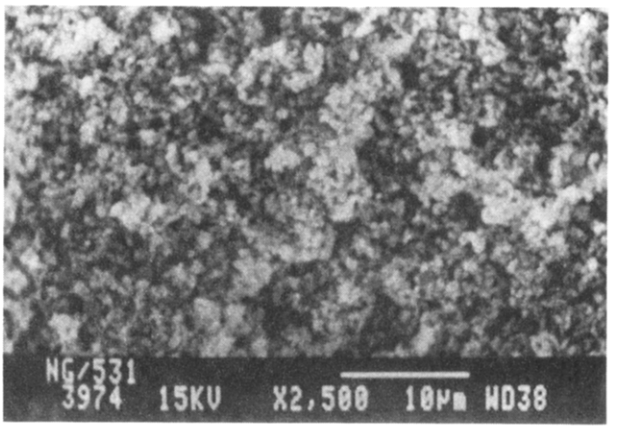

Figure 9. SEM photograph of IPN with PZnA at a magnification of 1500 times (reduced to 80% for publication).

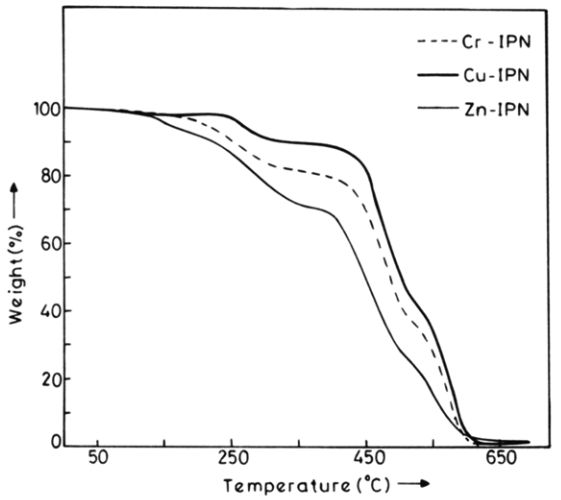

Figure 10. Thermal stability of chromium, copper, and zinc IPNs.

shows the complex structure. Figures 4–6 are the photographs of IPN[1,11,13] at a magnification of 1500 times, respectively (reduced to 80% for publishing). All the photographs show two phase morphologies of the IPN. This observation is a consequence of DSC results showing two T_g's (glass transition temperatures), characteristic of a two-phase system for IPN-1 (Figure 7).

Properties of IPNs with Different Metal Acrylates. Tables 8 and 9 explore the properties of IPNs from poly(chromium acrylate) (Cr-IPN), poly(zinc acrylate) (Zn-IPN), and poly(copper acrylate) (Cu-IPN). It is clear from Table 8 that the extractable material (%),

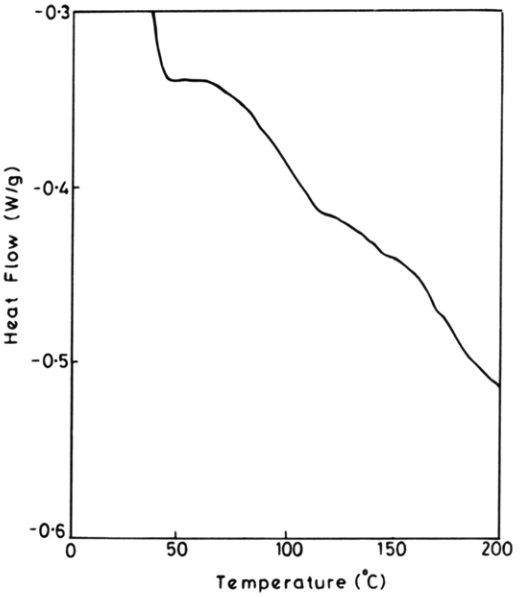

Figure 11. DSC curve of IPN with chromium acrylate (Cr-IPN).

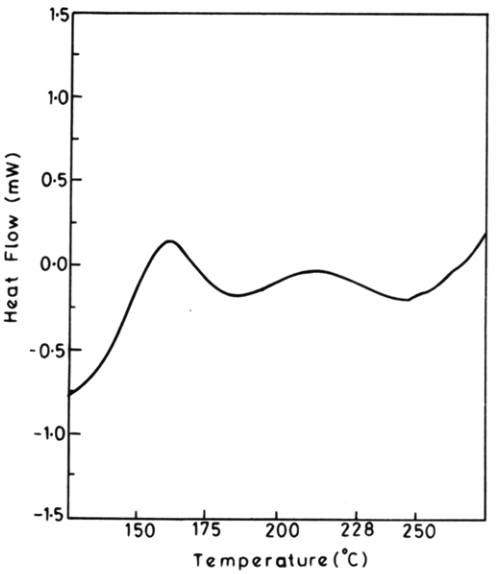

Figure 12. DSC curve of IPN with zinc acrylate (Zn-IPN).

swelling, and therefore M_c follow the order Zn-IPN > Cr-IPN > Cu-IPN.

The density of IPN also decreases with cross-linking.

Table 9 and Figure 10 depict the thermal stability of the IPN at 200, 300, and 400 °C which follows the following order: Cu-IPN > Cr-IPN > Zn-IPN.

All these results might be due to cross-linking in IPN resulting from grafting of poly(metal acrylate) with acrylonitrile in the following order: PCuA > PCrA > PZnA.

Although an exact explanation for this behavior cannot be put forward, it seems that the number of valance electrons (Cu, 2, 8, 18, 1: Cr, 2, 8, 13, 1; Zn, 2, 8, 18, 2) as well as filling of the 3d orbitals (Cu($3d^{10}$), Cr($3d^5$), and Zn($3d^{10}$)) is responsible for this behavior.

Figures 4, 8, and 9 show SEM photographs of Cu, Cr, and Zn IPNs at magnitifcations of 1500, 1000, and 1500 respectively (reduced to 80% for publishing). All these photographs show two distinct phases. This leads to the conclusion that in all three types of IPN the poly(metal acrylate) and poly(acrylonitrile) are incompatible; i.e. they are phase separated. Further, Figures 7, 11,

and 12 show DSC curves of Cu, Cr, and Zn IPNs. All the IPNs show two T_g values (Table 9), confirming the presence of phase separation in the IPNs.

Conclusion

The following conclusions were drawn:

1. The IPN is a grafted type of IPN.
2. For copper acrylate IPNs: M_c, swelling $\propto$ 1/cross-linking $\propto$ 1/[cross-linking agent], 1/[linear polymer], 1/[monomer II], [AIBN], $1/\eta_{int}$ of linear polymer.
3. For copper, chromium, and zinc IPNs the order of cross-linking and thermal stability is Cu-IPN > Cr-IPN > Zn-IPN.
4. All the IPNs show phase separation and two T_g values.

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