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INTERPENETRATING POLYMER NETWORK OF POLY(BISMUTH ACRYLATE) AND POLY(ARSENIC ACRYLATE): SYNTHESIS AND CHARACTERIZATION

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Key Words: IPN's, Poly(bismuth Acrylate), Poly(arsenic Acrylate), Morphology, Properties

ABSTRACT

IPN based on poly(bismuth acrylate) and poly(arsenic acrylate) have been synthesized by using BPO as initiator. Complex formation occurs through "polymer solvent" method indicating contraction of polymer coils through weak van der Waal's forces, by determining the value of mutual interaction constant (K_{AB}) in different solvents such as DMSO, DMF, dioxane. The scanning electron microscopy reveals a two phase morphology of both metal acrylates and the infrared spectrum indicates frequency of (>C=O) at 1640 cm^{-1}. The properties like percentage swelling, crosslink density, young's moduls are a direct function of linear polymer [polybismuth acrylate] and initiator [benzoyl peroxide] where as inverse function of monomer [arsenic acrylate] and crosslinker [divinylbenzene]. The differential scanning calorimeter (DSC) curve shows two glass transition temperatures of the IPN at 63°C and 79°C. The value of the activation energy, of IPN, calculated from thermogravimetric analysis is 10.25 KJ/mol.

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INTRODUCTION

Polymer chemistry, a significant branch of organic chemistry, is expanding vigorously because of unique properties of polymers such as being lightweight, having an advantage in rigidity, impact strength, and high temperature resistance. The manifold applications largly depend upon property of polymers which, in turn are modified in the form of block, copolymer, ion exchange resin, template polymer, starshaped polymer, crosslink polymer, etc. One of the attractive solutions of the polymer modification and crosslinking of two polymer is the synthesis of Interpenetrating Polymer Network (IPN) [1, 2]. IPN are composed of two (or more) chemically distinct networks held together by their trapped mutual entanglements rather than by covalent bond grafting. Crosslinked polymers are found in many and varied applications throughout the chemical industry including rubber, latexes, urethanes, epoxies, aqueous fluid absorbers, etc.

Millar [3] was the first to have used the term IPN, which was pursued by Sperling *et al* [4-6]. and Frisch *et al.* [7, 8], who presented papers on synthesis, morphology, and mechanical behavior on IPN's. There is splendid scientific literature concerning IPN's based on polyurethanes [9, 10], epoxy resins [11], PVC/polybutadiene-co-AN based latex IPN, phenolformaldehyde resin [12]. Reza *et al.* [13] have reported the synthesis and morphology of IPN containing copolymers of methylene bis-acrylamide and vinyl ferrocene. Recently the reports on synthesis of IPN using only one metal acrylate such as zinc, copper, chromium with vinyl monomers have been published from the lab [14, 15, 36].

However, in spite of this interest, very little systematic data has appeared, especially concerning the effect of molecular weight and concentration of dispersed phase on the morphology and properties of the system. Therefore, the main aim of this work is to synthesize IPN's containing poly (bismuth acrylate) and poly (arsenic acrylate) and to study the effect of the variation of polymer I/polymer II/crosslinker/initiator on the morpholoy and crosslinking of the resulting multiphase system.

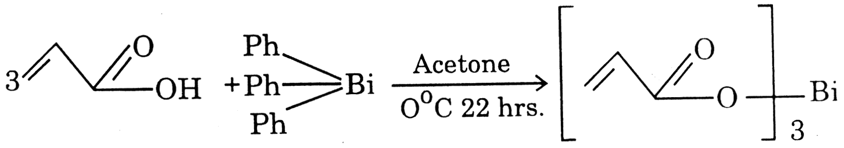
EXPERIMENTAL

Methanol, dimethylformamide, dimethylsulphoxide, benzene, toluene, acetone and divinyl benzene are used. Benzoyl peroxide (BPO) is recrystallized in chloroform (M.P = 103°C).

Synthesis of Metal Acrylates

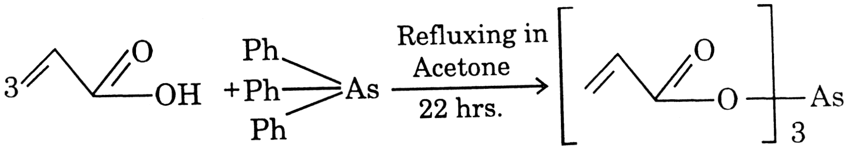
Bismuth Acrylate

The bismuth acrylate is synthesized by the reported method [16] by refluxing a suspension of acrylic acid and triphenyl bismuth (30 wt% stoichiometric excess) (Merck no. 821192) using acetone as a solvent for 22 hours in an ice bath. The evaporation of excess solvent yielded bismuth acrylate.



Arsenic Acrylate

The arsenic acrylate was synthesized by the reported method [17], by refluxing suspension of acrylic acid and triphenyl arsine (30 wt% stoichiometric excess), (Merck no. 808653) using acetone as solvent for 22 hourrs. The evaporation of excess solvent yielded arsenic acrylate.



Synthesis of Poly(bismuth Acrylate)

Bismuth acrylate was polymerized by using BPO as a radical initiator, in DMF at 85°C ± 1 for 1 hour.

Synthesis of IPN

A series of 16 IPN's have been studied by taking a calculated amount of poly (bismuth acrylate) (1.61-5.91) (base M) × 10^{-6}mol/100ml IPN 1-5, (Table 3); (1.07-5.39) × 10^{-6} mol/100ml of arsenic acrylate IPN 6-10, (Table 4); (2.86-8.26) × 10^{-6}mol/100 ml of BPO IPN 11-13, (Table 5), as initiator and (1.51-4.61) × 10^{-6}mol/100 ml, IPN 14-16, (Table 6), of DVB was dissolved in DMF and the contents were kept for 1 hour at 85°C ± 1 under a blanket of nitrogen.

Finally, the IPN was vacuum dried until a constant weight was obtained. The principal chemical variables include a systematic variation of a concentration of poly (bismuth acrylate), arsenic acrylate, divinyl benzene (DVB), and benzoyl peroxide (BPO).

Characterization of IPN

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

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

Swelling Properties

Before proceeding to the measurements of swelling of polymer network in different solvents, the soluble or uncrosslinked component of IPN was removed with the help of soxhlet extractor. The percentage extractable material has been calculated according to the following Equation (1).

$$\% \text{ extractable material} = \frac{W_b - W_a \text{ x } 100}{W_a} \qquad (1)$$

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

$$\% \text{ Swelling} = \frac{W_s - W_d}{W_d} \times 100 \qquad (2)$$

where W_s = weight of swelled IPN and W_d = weight of dry IPN.

Swelling data has been calculated by soaking the sample in different protic and aprotic solvents such as dimethyl formamide, dimethylsulphoxide, dioxane, benzene, and toluene until an equilibrium weight was achieved (~ 24 hours). Weight measurments have been 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 an equilibrium weight was achieved. The percentage swelling is calculated according to the following relationship [18].

The degree of crosslinking is defined as the number of crosslinks per unit volume of polymer. The following relationship is used for the calculation of a degree of crosslinking

$$C = \frac{n}{2} = \frac{d}{2M_c} \tag{3}$$

where C = degree of crosslinking, d = density of network, Mc = average mol wt. between crosslinks, and n = crosslink density.

Crosslink Density

The crosslink density of the network was determined by using the swelling data of IPN's in DMF with the help of the Flory-Rehner Equation (4) [19, 20].

$$\frac{1}{M_c} = \frac{-\ln\ (1-V_p) + V_p + X_{12}\ V_p^2}{\rho V_1,\ (V_p^{1/3} - V_p/2)} \tag{4}$$

where M_c = average mol wt of network between crosslinks, ρ = density of network, V_1 = molar volume of solvent, V_p = volume fraction of polymer in swollen gel, and X_{12} = polymer solvent interaction parameter, calculated as 0.342 by the following expression (Equation 5) [21].

$$X_{12} = \frac{B + V_1}{RT}\ (\delta_p - \delta_s)^2 \tag{5}$$

where δ_p and δ_s = solubility parameters of polymer and swelling solvent and B = lattice constant.

The crosslink density further paves a path for determining Young's modulus or stress-strain relationship by the following Equation (6) [22].

$$E = 3n\ RT\ (V_p)^{1/3} \tag{6}$$

where V_p = vol. fraction of polymer in swollen gel, n = crosslink density, and R ,T are constant.

Complex Formation

The ability of the two polymers to form a complex depends upon the solvent, on the concentration ratio of polymers in the mixture, on their total concentration and on time. Preparation of polymer samples, their characterization, procedure used in measurement have been reported in earlier papers [23-25].

Solutions used in viscosity measurements were prepared in the following way. The Poly [bismuth acrylate] solution was used as the solvent and dissolved to give a series of solutions having concentrations ranging from 2.5×10^{-4} to 10×10^{-4} g cm^{-3}. After dissolution and filtration, the second polymer poly [arsenic acrylate] (conc. 10×10^{-4} g/cm^3) was dissolved in these solutions.

To find out the strength of interaction between polymers, the interaction constant K_{AB} of a mixture of stereo complex polymers of poly(bismuth acrylate) and poly(arsenic acrylate) is evaluated. In this study, the determination of interaction coefficient K_{AB} at 60°C is determined. It characterizes mutual interaction between two polymers at this temperature as an analogy of a solution of binary mixture of compatible polymers in a common solvent. For this purpose, the method of polymer solvent was employed [26-33]. According to this method, the intrinsic viscosity of the polymer A, $(\eta_A)_B$ [poly arsenic acrylate) is determined in a number of solutions of different concentration of polymer B poly (Bi acrylate) which serves as a series of solvents and viceversa for $(\eta_A)_b$ we have [34].

$$[\eta_A]_B = [\eta_A]/[\eta_r]_B \; [1 + 2K_{AB} \; [\eta_B] \; C_B \; + \ldots.] \tag{7}$$

where $(\eta_A)_B$ in the relative viscosity of the polymer B at concentration (C_B). (C_B), and $[\eta_A]$, $[\eta_B]$ are intrinsic viscosities of the polymer A and B.

The constant K_{AB} is a criterion of interaction. It may be obtained from the plot of f vs the reduced concentration $C = [\eta_B]C_B$ giving directly K_{AB} from the intercept or the y axis.

$$f = \frac{[\eta_A]_B \; [\eta_A]}{[\eta_r]_B} - 1/2$$

SEM Morphology

The morphology of the IPN’s is studied by the scanning electron microscopy (SEM) which has a resolution of 50A° and depth of field 30μ. Samples were mounted on a SEM stub by graphite adhesive paste and coated with gold is a SEMcoating unit. The samples were then scanned in a JEOL JSM 840 A scanning e microscope. SEM also helps to estimate the percentage of metals present in the sample.

Thermal Properties

Measurements of glass transition temperature was carried out with a differential scanning calorimeter general V2.2A Dupont Model 9900. DSC curves were recorded under nitrogen atmosphere at a flow rate of 10°C/min. The sample weight was 4.5±0.1mg.

Thermo-Gravimeteric Analysis (TGA)

Thermogravimeteric analysis was carried on TGA V5 1A Dupont 2100 at heating range of 10°C/min under nitrogen atmosphere. The activation energy (Ea) and order of a reaction was calculated from the Coats and Redfern Equation (8) [35].

$$\log\ g\ (\alpha)/T^{2} = \frac{Ea}{2.3RT} + \log.\ ZA/_{BE}\ (1—{}^{2RT}/_{Ea}) \qquad (8)$$

$$g = —\log\ [(1—\alpha)1/n] \qquad (9)$$

where Z = pre exponential factor, T = temperature, B = linear heating rate, and R = gas constant.

The plot of log [g α/T^{2}] versus 1/T x 103 gives a linear curve, whose slope is equal to $-Ea/2.3RT$, and its intercept corresponds to $\log_{10}$ 2A/BΔE ($1-2RT/Ea$).

RESULTS AND DISCUSSION

IR spectrum of IPN (Figure 1) indicates characteristic frequencies of carboxylic groups (>C=O) at 1640 cm^{-1}; around 3000 cm^{-1} of aromatic ring of DVB.

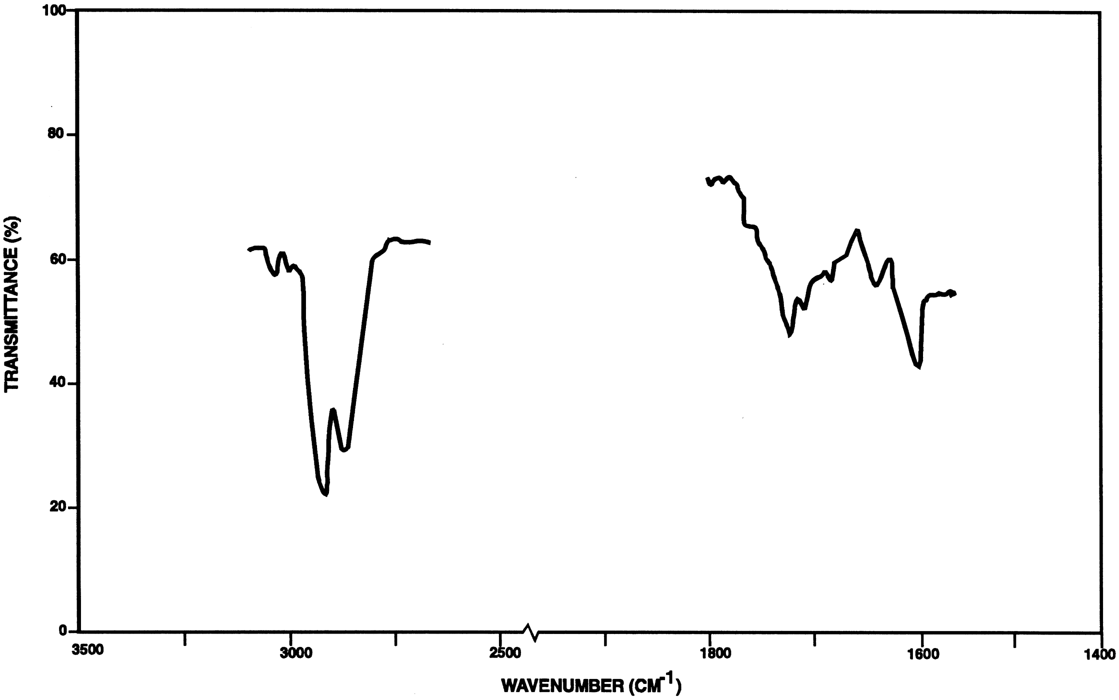
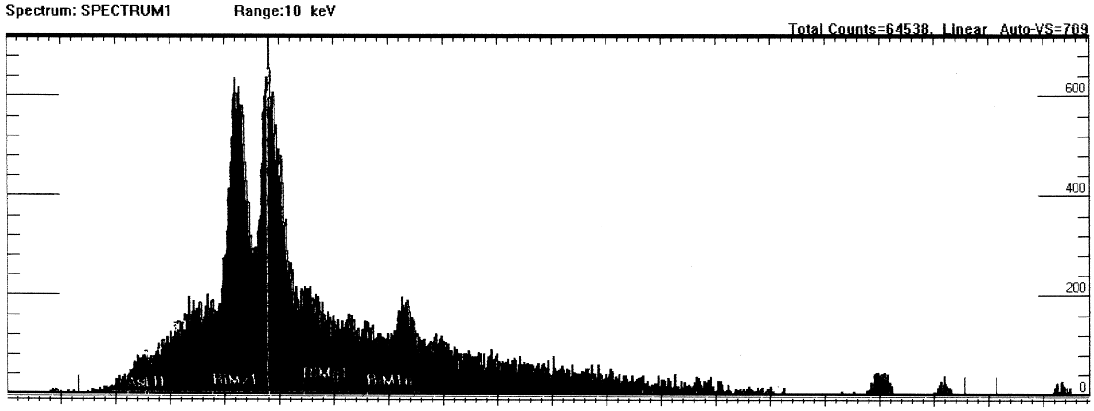


Figure 1. IR spectrum of IPN.

Arsenic and Bismuth were confirmed by spot analysis and also through SEM (Figure 2).

Complex Formation

The determination of K_{AB} values, which are associated with the interaction of unlike polymer molecules in the field of shear forces, is similar to the Huggins coefficient K_A and K_B is calculated by complex formation methods. In general, the Huggins coefficient originates from a superposition of several types of interactions, hydrodynamic and thermodynamic interactions being the most important. The thermodynamic contribution includes the intramolecular excluded volume effect, resulting in an expansion of the coil and intramolecular excluded volume effect, which results in the contraction of the coil. The K_{AB} values characterizes the intensity of complexation in different solvents namely DMSO, DMF, dioxane. The results are summarized in (Table 1). The value of mutual interaction coefficient K_{AB} for the given system A = PAsA and B = PBiA was determined by extrapolating these lines. The common intercept was obtained



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[A N A L Y S I S   R E P O R T]

GENERAL CONDITIONS
------------------
 Result File       : SPECTRUM1
 File Version      : 1
 Background Method : Auto
 Decon Method      : Gaussian
 Decon ChiSquared  : 95.31
 Analysis Date     : 17-MAY-99
 Microscope        : SEM
 Comments          :

ANALYSIS CONDITIONS
-------------------
 Quant. Method        : XPP/ASAP
 Acquire Time         : 100 secs
 Normalization Factor: 100.0

SAMPLE CONDITIONS
-----------------
 kV                  : 15.0
 Beam Current        : 150.0 picoAmps
 Working Distance    : 39.0 mm
 Tilt Angle          : 0.0 Degrees
 TakeOff Angle       : 40.0 Degrees
 Solid Angle*BeamCurrent: 1.2


Element Line   Weight%        Cnts/s   Atomic%
-----------------------------------------------
As      La     13.44           13.21    30.21
Bi      Ma     86.56          115.41    69.79

Total          100.00
```

Figure 2. Spot analysis curve of IPN 3.

on the y axis, and K_{AB}=0.28 (DMSO); 0.22 (DMF); 0.16 (Dioxane). The K_{AB} values are low in comparision to those reported earlier [34, 35]. These values indicate that the interaction between PAsA and PBiA is weak and involves weak van der Waal's forces due to intramolecular excluded volume effect resulting in contraction of the coil. Study of (Table 1) shows that the value of [PAsA]/PBiA increase as concentration of PBiA increase significantly in DMSO, DMF and Dioxane. This indicates that there is a decrease in the dimension of the molecules of PAsA in presence of PBiA. It is therefore, concluded that the molecular dimension decreases significantly in DMSO, and to a lesser extent in DMF and dioxane. The higher value of K_{AB} in DMSO (K_{AB} = .28) in comparision to DMF (K_{AB} = .22) and dioxane (K_{AB} = .16), shows that the strength of complexation is stronger in DMSO, than DMF and dioxane (weaker), and is related to the dielectric constant of the solvents.

After the formation of the complex, emphasis is placed on the effect of poly [BiA], [AsA], DVB, Benzoyl peroxide on properties such as swelling, crosslink density, young's modulus, and phase behavior.

The results of swelling in various solvents such as DMF, DMSO, dioxane, benzene, toluene are given in (Table 2). A high percentage of extractable material is shown in (Table 2), which may be due to insufficient crosslinking. Poor or no grafting of linear polymer to the other crosslinked polymer can also be the reason for the above result. Almost all the samples show swelling, the crosslink density (1/Mc) is an inverse function of the percentage of metals in the sample.

Effect of Composition

The effect of the composition of [PBiA] follows a logical trend since an increase in [PBiA] results in increased swelling and 1/Mc value (Table 3). This implies that the presence of [PBiA] restricts crosslinking of [PAsA]. This restriction is due to an overall decrease in the concentration of crosslinking sites of [PAsA]. As the [poly bismuth acrylate] increases the probability of grafting by AsA also increases, which produces some degree of crosslinking in PBiA, thus suppressing the crosslinking of AsA to some extent. Also, it is observed that increase in concentration of PBiA increases the value of young's modulus (Table 3). This result predicts that increase in [PBiA] increases the modulus value (4.01×10^5 - 5.56×10^5) dynes/cm^2 and therefore, the mechanical strength of the polymer. A similar explanation has been given for the inverse function of percentage swelling and crosslink density with [AsA] (Table 4).

TABLE 1. Intrinsic Viscosity in Polymer Solvent (PBiA/PAsA), Temperature = 30°C ± 1.

Solution in DMSO

[PBiA] x 10^{-4} (Base M)	η[PBiA] (B)	η[PAsA] (A)
2.5	.05	.08
5.0	.08	.09
7.5	.10	.12
10.0	.13	.14

Solution in DMF

[PBiA] x 10^{-4} (Base M)	η[PBiA] (B)	η[PAsA] (A)
2.5	.04	.02
5.0	.05	.06
7.5	.07	.11
10.0	.10	.17

Solution in Dioxane

[PBiA] x 10^{-4} (Base M)	η[PBiA] (B)	η[PAsA] (A)
2.5	.02	.03
5.0	.03	.05
7.5	.06	.08
10.0	.08	.13

TABLE 2. Percent Swelling of IPN in Different Solvents, % Extractable Material and % Metal Content (Determined by SEM)

Sample no.	DMF	DMSO	Dioxane	Toluene	Benzene	% Extractable material	% Metal Content Bi	As
IPN-1	40%	36%	30%	23%	21%	40%	—	—
IPN-2	56%	49%	46%	33%	24%	39%	—	—
IPN-3	60%	57%	48%	37%	32%	38%	86.56	13.44
IPN-4	72%	65%	53%	42%	38%	45%	—	—
IPN-5	79%	73%	61%	50%	42%	32%	10.05	5.21
IPN-6	96%	88%	81%	68%	62%	81%	—	—
IPN-7	72%	65%	60%	57%	51%	58%	48.88	51.12
IPN-8	69%	58%	50%	46%	41%	28%	—	—
IPN-9	62%	51%	47%	41%	30%	22%	—	—
IPN-10	48%	42%	38%	32%	22%	61%	—	—
IPN-11	68%	61%	53%	49%	32%	68%	—	—
IPN-12	87%	78%	71%	60%	59%	71%	—	—
IPN-13	106%	92%	84%	69%	66%	19%	—	—
IPN-14	98%	81%	72%	68%	61%	31%	—	—
IPN-15	66%	61%	55%	48%	36%	56%	—	—
IPN-16	59%	52%	49%	37%	29%	62%	—	—

TABLE 3. Effect of [PBiA] (base M) on IPN Properties

S. No.	[PBiA] baseM $\times 10^{-6}$ mol/100ml	% yield	% swelling in DMF	1/Mc in DMF gm/cm^3	Young's Modulus (dynes/cm^2)
IPN-1	1.61	21	40	74	4.01×10^5
IPN-2	2.68	24	56	92	4.69×10^5
IPN-3	3.76	32	60	96	4.84×10^5
IPN-4	4.84	38	72	112	5.44×10^5
IPN-5	5.91	42	79	117	5.56×10^5

[AsA] = 1.07×10^{-6} mol/100ml.

[BPO] = 4.13×10^{-6} mol/100 ml.

[DVB] = 2.30×10^{-1} mol/100ml.

Temperature = 85^{0}C ± 1

Time = 1 hr.

TABLE 4. Effect of [AsA] on IPN Properties

S. No.	[AsA]$\times 10^{-6}$ mol/100 ml	% yield	% swelling in DMF	1/M_c in DMF gm/cm^3
IPN-6	1.07	81	96	133
IPN-7	2.15	58	72	109
IPN-8	3.23	28	69	106
IPN-9	4.31	22	62	99
IPN-10	5.39	61	48	96

[PBiA] (base M) = 1.61×10^{-6} mol/100 ml.

[DVB] = 2.30×10^{-1} mol/100 ml.

[BPO] = 4.13×10^{-6} mol/100 ml.

Temperature = 85^{0}C ± 1

Time = 1 hr.

Effect of Initiator [BPO]

Table 5 presents data on the effect of (benzoyl peroxide) on the swelling and crosslink density of IPN. The data shows that both swelling and crosslink density increases with an increase of [BPO].

Effect of Crosslinker (DVB)

(Table 6) shows that as [DVB] increases, the percentage of extractable material increases. The reason for this is that a higher concentration of crosslinking agent increases crosslinking and consequently, percentage swelling. The percentage swelling of IPN in different solvents and crosslink density (1/Mc) is inverse function of [DVB]. This shows that an increase of [DVB] increases the crosslinking level, which results in a decrease of swelling and cross-link density.

Morphology and Thermal Properties

The SEM study of IPN shows a two phase morphology at 2000 times magnification, of both metal acrylates, crosslinked with each other, (Figure 3).

TABLE 5. Effect of [BPO] on IPN Properties

S. No.	$[AsA] \times 10^{-6}$ mol/100 ml	% yield	% swelling in DMF	$1/M_C$ in DMF gm/cm^3
IPN-11	2.06	68	68%	105
IPN-7	4.13	58	72%	109
IPN-12	6.19	71	87%	124
IPN-13	8.26	19	106%	143

[PBiA] (base M) = 1.61×10^{-6} mol/100 ml.

[PAsA] = 1.07×10^{-6} mol/100 ml.

[DVB] = 2.30×10^{-1} mol/100 ml.

Temperature = 85^0C ± 1

Time = 1 hr.

TABLE 6. Effect of [DVB] on IPN Properties

S. No.	DVB mol/100ml x 10^{-1}	% yield	% swelling in DMF	$1/M_c$ gm/cm^3
IPN-14	1.15	31%	98	135
IPN-7	2.30	58%	72	109
IPN-15	3.46	56%	66	102
IPN-16	4.61	62%	59	95

[PBiA] (base M) = 1.61 x 10^{-6} mol/100ml.

[AsA] = 1.07 x 10^{-6} mol/100ml.

[BPO] = 4.13 x 10^{-6} mol/100ml.

Temperature = 85°C ± 1

Time = 1 hr.

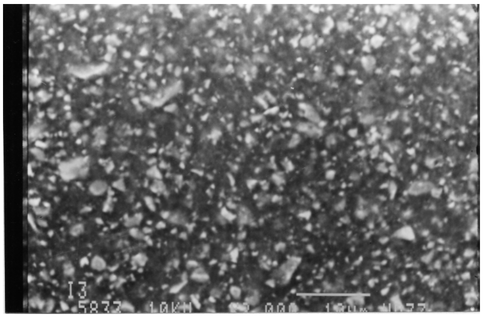

Figure 3. SEM photograph of IPN 3 at magnification of 2000 times as shown.

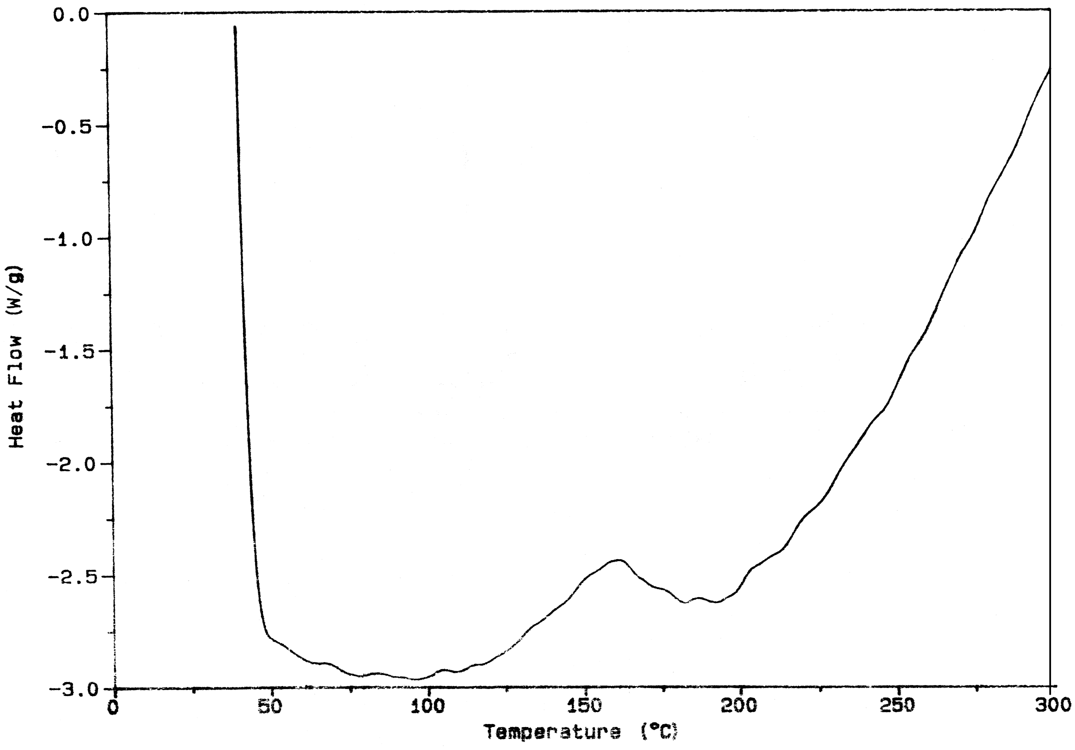

Figure 4. DSC curve of IPN.

The white dots in (Figure 3) represent the PBiA network whereas, the dark continous phase is due to PAsA. The DSC result (Figure 4) further confirms the above observation by showing a two glass transition temperature of IPN at 63°C, 79°C; thus confirming that it is a semi IPN.

Thermogravimetric Analysis

The thermogravimetric result (Figure 5) of the IPN sample containing (PBiA-AsA) is stable up to 438.80°C and started losing weight above this temperature. Rapid decomposition is observed at 450°C. Weight loss of about 37% is observed at 470°C.

The activation energy calculated from the slope of linear graph plotted between —log[log (1—α)/T^2] vs. 1/T $\times 10^3$ is 10.25 KJ/mol (Figure 6).

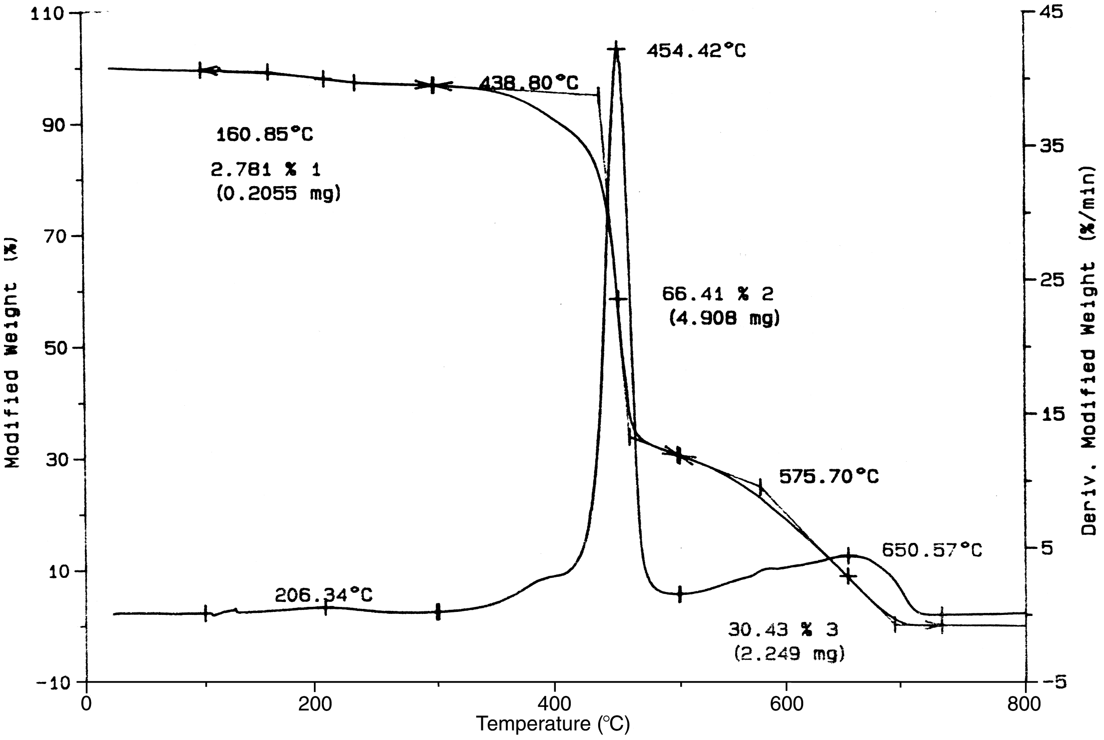

Figure 5. TGA of IPN.

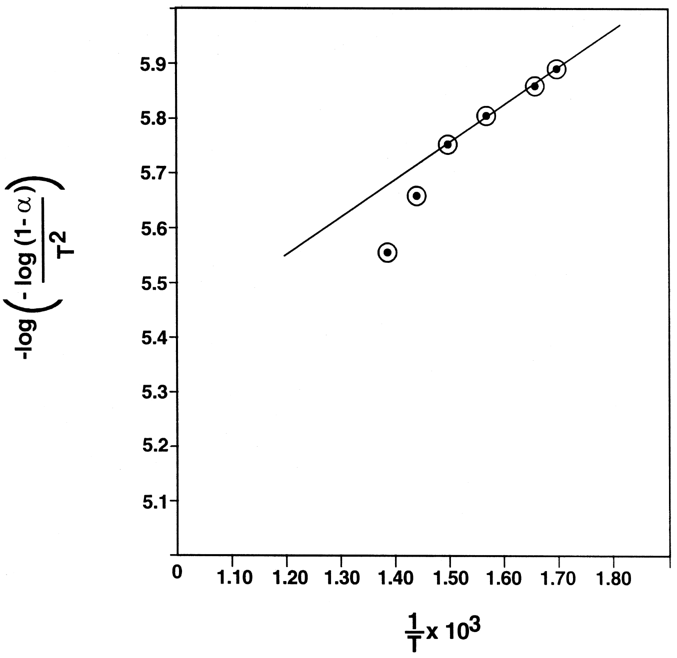

Figure 6. Graph between-log $[\log(1-\alpha)/T^2]$ Vs1/T x 10^3.

CONCLUSION

The conclusions are as follows :

Complex formation occurs between the two polymer coils which undergo contraction involving the van der Waals interaction.

Crosslink density is a direct function of [Linear Polymer], [Initiator] where as inverse function of [Monomer] and [DVB].

IPN's show phase separation and two Tg values.

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