Solution Properties of Methyl Methacrylate–Acrylonitrile Copolymers

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SYNOPSIS

Characterization of methyl methacrylate–acrylonitrile copolymers is done through viscosity, swelling, and differential refractometric studies. Viscosities of the copolymers and homopolymers were determined at 30, 40, and 50°C. The activation parameters of viscous flow, voluminosity, and shape factor were also calculated. The average shape factor was observed to be 2.5 ± 0.005 for all copolymer systems. Viscosity molecular weights were calculated, and from intramolecular expansion factor (α), it was observed that copolymers are less flexible than are homopolymers. dn/dc values obtained from differential refractometry are in good agreement with those calculated theoretically. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Methyl methacrylate–acrylonitrile copolymerization has been extensively studied for random, block, as well as graft copolymers.[1-4] Various initiation methods[1-3] have been used and extensive characterization through different techniques has also been carried out. However, viscometric characterization has received comparatively less attention for this system. Hence, in the present study, we have characterized the random copolymers of methyl methacrylate (MMA) and acrylonitrile (AN) through viscometric, swelling, and refractive index studies. The synthesis and optimization of the polymerization conditions has been reported earlier.[5] The reaction medium used for the synthesis was toluene, a comparatively cheaper solvent.

EXPERIMENTAL

The synthesis of MMA–AN copolymers was carried out using benzoyl peroxide initiator and toluene medium, as discussed earlier.[5] The reaction was car-

ried out at 75°C for 6 h. Methanol was used for precipitation of the product.

Viscosity Measurements

Viscosity measurements of the dilute solutions of the copolymers in DMF, DMSO, and acetone were carried out using an Ubbelohde dilution viscometer suspended in a thermostated bath with ±0.05°C temperature control. The solution concentrations ranged from 0.3 to 1.0 g/dL. Measurements for each solution were repeated five to six times. Densities of the solutions at different temperatures were assumed to be those of solvents at that temperature.[6] No kinetic energy corrections were made because the efflux flow times of the solvents were more than 100 s. Since intrinsic viscosities of the copolymer solutions are below 2.0 dL/g, the effect of shear rate was negligible. Viscosity molecular weights were computed by using the relationship

$$|\eta| = KM^a$$

and earlier reported K and a values in DMF and acetone.[7-9]

Swelling Behavior

Swelling behavior of the copolymers of MMA–AN, with various compositions, was studied on approx-

imately uniform particle-size powdered samples. The swelling in different solvents was calculated as

% swelling

$$= \frac{\begin{array}{c}\text{weight of the swollen polymer}\\ - \text{ weight of the dry polymer}\end{array}}{\text{weight of the dry polymer}} \times 100$$

Differential Refractive Index

Differential refractive indices were determined at 25°C using DMF as solvent and a Brice Phoenix Differential Refractometer with a 632.8 nm filter. The difference in refractive index of a polymer solution and solvent was determined for five different concentrations. The difference in displacement was calculated as

$$d = (d_2 - d_1)_{\text{solution}} - (d_2 - d_1)_{\text{solvent}}$$

where d_2 and d_1 refer to the measurements of displacement of 0° and 180°, respectively. The difference in refractive index was given as $\Delta n = \Delta d K_c$, where K_c is a calibration constant for the instrument and was calculated at 25°C using aqueous potassium chloride solutions.

RESULTS AND DISCUSSION

Viscosity Studies

The effect of temperature on the hydrodynamic behavior of dilute polymer solutions can be obtained

by the temperature dependence of the intrinsic viscosity in both the solvents DMF and DMSO (Table I and Fig. 1). It is observed that the intrinsic viscosity decreases, in general, with increase in temperature, though the effect is more pronounced in DMF than in DMSO. $|\eta| - T$ plots are always linear, with the negative slope indicating that the polymer coils are not swelling to a great extent and that a lower critical solution temperature is exhibited by the systems, particularly in DMF. This is due to the decreased thermodynamic affinity with increased temperature. Moreover (Table I), it can be recognized that as the mole fraction of AN in the copolymer increases the intrinsic viscosity generally shows a small decrease, and when the MMA : AN ratio is $\sim$ 1, it goes on increasing. From the values of intrinsic viscosity and molecular weights, it is observed that molecular weight is not the only factor affecting intrinsic viscosity but also the solute–solvent interaction and, hence, the chemical composition, the homogeneity, and the length of sequences of chemically identical monomer units. Similar observations were made by Morimto and Okamoto[10] and others.[11]

The well-known Frenkel–Eyring equation for viscous flow can be written as

$$\eta = (N_h/V)\exp(\Delta G_{\text{vis}}^{\ddagger}/RT) \qquad (1)$$

where V is the molar volume and other quantities have their usual significance. This equation can be rewritten as

$$\ln(\eta V/Nh) = (\Delta H_{\text{vis}}^{\ddagger}/RT) - (\Delta S_{\text{vis}}^{\ddagger}/R) \qquad (2)$$

Table I   Intrinsic Viscosity and Viscosity Molecular Weights of Homo- and Copolymers of AN and MMA

| Sample No. | Mol Fraction of AN | | Intrinsic Viscosity in DMF (dL/g) | | | Intrinsic Viscosity in DMSO (dL/g) | | | Mol. wt.[a] $(\bar{M}_v \times 10^{-3})$ |
	Taken in Reaction Mixture	Found in Copolymer	30°C	40°C	50°C	30°C	40°C	50°C	
A$_1$	0.35	0.32	0.38	0.35	0.33	0.32	0.31	0.30	8.4
A$_2$	0.45	0.36	0.30	0.28	0.26	0.26	0.25	0.26	6.94
A$_3$	0.52	0.40	0.31	0.31	0.30	0.30	0.29	0.29	7.63
A$_4$	0.62	0.45	0.30	0.26	0.26	0.30	0.29	0.29	6.91
A$_5$	0.71	0.59	0.58	0.55	0.50	0.58	0.58	0.55	17.64
A$_6$	0.76	0.62	0.66	0.63	0.53	0.61	0.61	0.50	30.51
A$_7$	0.83	0.72	1.16	1.00	0.91	1.00	1.10	1.00	38.86
PAN	—	—	1.16	1.10	1.05	1.14	1.11	1.09	72.72[b]
PMMA	—	—	0.35	0.36	0.36	Insoluble			40.30[c]

[a] Calculated using intrinsic viscosities and K and a values for copolymers at 25°C in DMF.
[b] At 30°C in DMF.
[c] At 30°C in acetone.
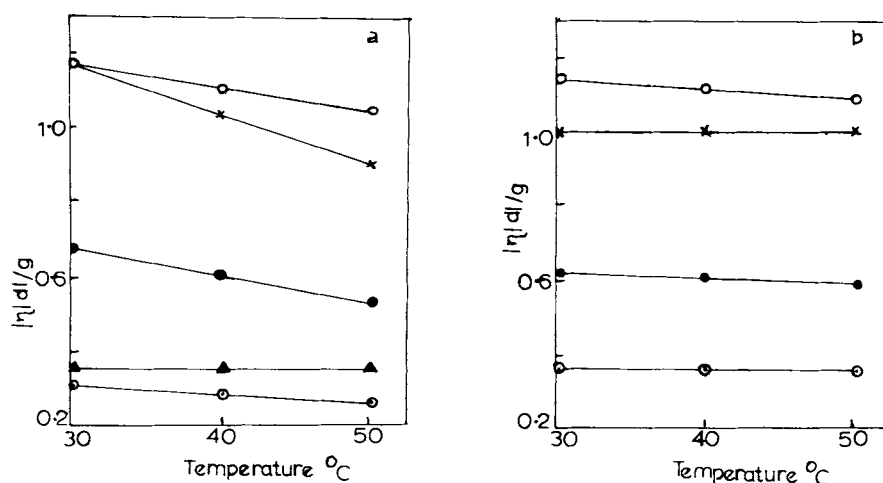
Figure 1   Effect of temperature on intrinsic viscosity of copolymers: (a) in DMF; (b) in DMSO; ($\odot$) A_2, ($\bullet$) A_6; ($\mathbf{x}$) A_7; ($\bigcirc$) PAN; ($\blacktriangle$) PMMA.

where $\Delta H_{vis}^{\ddagger}$ and $\Delta S_{vis}^{\ddagger}$ are enthalpy and entropy for the viscous flow. Representative plots of $\ln(\eta V/Nh)$ vs. T^{-1} are given in Figure 2. Polyacrylonitrile (PAN), poly(methyl metacrylate) (PMMA), and all copolymers at all concentrations and in both solvents showed a linear relationship with a correlation
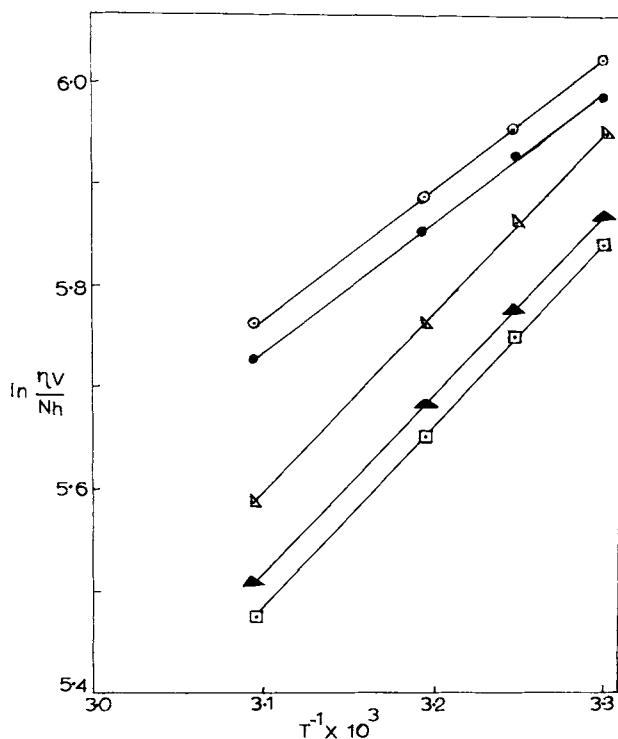
Figure 2   Plots of $\ln \eta V/Nh$ against $1/T$ for 0.6 g/dL solutions in DMSO: ($\blacktriangle$) A_1; ($\boxdot$) A_2; ($\triangle$) A_3; in DMF: ($\bullet$) A_5; ($\odot$) A_6.

coefficient of 0.9990 ± 0.0006. The calculated values of $\Delta H_{vis}^{\ddagger}$ and $\Delta S_{vis}^{\ddagger}$ are given in Table II. It is observed that $\Delta H_{vis}^{\ddagger}$ of all systems in a particular solvent are more or less constant, though they differ from the other solvents. The average $\Delta H_{vis}^{\ddagger}$ in DMF and DMSO was found to be 10.65 ± 0.29 and 15.20 ± 0.04 kJ mol^{-1}, respectively. These values are not large and their constancy seems to indicate that the polymers are not cross-linked. The $\Delta S_{vis}^{\ddagger}$ values, however, are not constant and tend to a higher value as the concentration decreases. But these values in DMSO are very small—of the order of a Joule, though in DMF, the values are higher by an order of magnitude and are comparable to some values reported earlier.[12] But a critical look of these values indicates that in both solvents as the concentration of AN in the copolymer increases the $\Delta S_{vis}^{\ddagger}$ tends to decrease, indicating a reasonably ordered system.

Figure 3 shows that the free energy of activation of the viscous flow, $\Delta G_{vis}^{\ddagger}$, is reasonably independent of temperature. In two solvents DMF and DMSO, the values are certainly different but the difference is only a few percent and thereby preclude any further discussion.

The Frenkel–Eyring equation has also been written in the form

$$\eta = A \exp(\Delta G_{vis}^{\ddagger}/RT),$$

where the preexponential factor A is difficult to determine. As we mentioned in an earlier paper,[12] a comparison with eq. (1) indicates that $A = Nh/V$. It has been suggested that $A \approx 10^{-3}$ poise. With appropriate units, Nh is 10^{-3}, signifying that V is
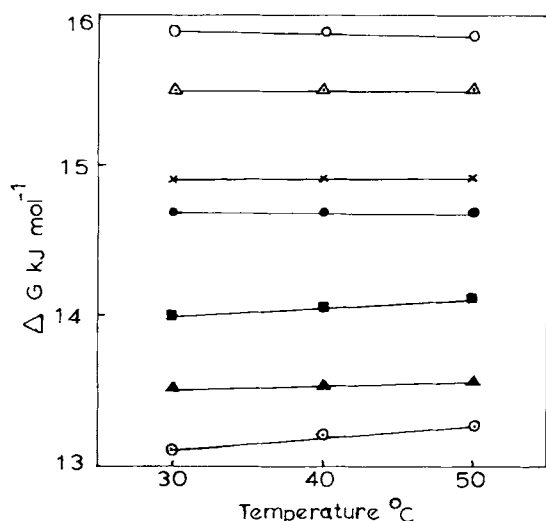
Figure 3 Effect of temperature on $\Delta G_{vis}^{\ddagger}$ in DMF (concentration 0.5 g/dL): (■) PAN; (▲) A$_5$; (⊙) A$_4$; in DMSO (concentration 0.5 g/dL): (●) A$_1$; (x) A$_3$; (△) A$_7$; (○) PAN.

1 mL. This seems unlikely and, hence, we want to stress the point once again that eq. (1) must be used to calculate activation parameters of viscous flow with V as the molar volume of the solvent.

The intramolecular expansion factor for the copolymer solutions was calculated from the intrinsic viscosity measurements in θ solvents at 30°C using the $\alpha^3 = |\eta|/|\eta|_\theta$ relationship. Various θ solvent compositions and corresponding intrinsic viscosities are given in Table III. The spatial distribution in the actual molecule is assumed to be expanded uniformly by the factor α as the result of intramolecular interactions. From the results obtained (Table III), it is observed that the intramolecular expansion

factor for homopolymers of MMA and AN is higher than that for the copolymers of MMA and AN, indicating that the copolymers are more rigid than are the homopolymers. The variation in the composition of the copolymers does not affect α considerably. Viscosity molecular weights of the homopolymers and copolymers were calculated from intrinsic viscosities using K and a values from the literature. Inagaki et al.[7] reported K and a values as 2.96 $\times 10^{-4}$ dL/g and 0.74, respectively, for PAN in DMF at 30°C. Cohn-Ginsberg et al.[8] reported K and a values as 7.7 $\times$ 10^{-5} dL/g and 0.7, respectively, for PMMA in acetone at 30°C. Molecular weights of copolymers were determined by using the K and a values of 3.92 $\times$ 10^{-4} dL/g and 0.75 reported by Clealand and Stockmayer[9] for the copolymers. The results are given in Table I.

The relative viscosity data were used to calculate the equivalent hydrodynamic volume (voluminosity V_e), a measure of size of a solvated polymer molecule at infinite dilution. Narang and Garg[13] determined the shapes of protein molecules (natural polymers) in solution. The method was further applied for the copolymers.[12] In the present study, the same procedure was followed for the determination of Ve by plotting, $Y = [(\eta_r^{0.5} - 1)/C(1.35\eta_r^{0.5} - 0.1)]$ vs. C g cm^{-3} and extrapolating to $C = 0$ to get Ve. The voluminosity (mL/g at infinite dilution) is a function of temperature and is a measure of the volume of solvated polymer molecules. As the temperature increases, the solvation decreases and, hence, Ve decreases. Lower values of Ve in DMSO indicate that DMSO acts as a poorer solvent for the polymers in comparison with DMF. From $|\eta| = \nu Ve$, the shape factor[14] ν was calculated. A few representative plots for the determination of Ve are illustrated in

Table II Entropy $\Delta S_{vis}^{\ddagger}$ and Enthalpy $\Delta H_{vis}^{\ddagger}$ of Activation for the Viscous Flow of the MMA–AN Copolymers (Concentration of the Solutions 0.5 g/dL)

Sample No.	$\Delta H_{vis}^{\ddagger}$ (kJ mol^{-1})		$-\Delta S_{vis}^{\ddagger}$ (J mol^{-1} deg^{-1})	
	In DMF	In DMSO	In DMF	In DMSO
A$_1$	9.97	15.06	10.65	−1.17
A$_2$	10.27	15.17	9.45	−1.71
A$_3$	9.64	14.87	11.58	0.17
A$_4$	9.66	15.21	11.33	−1.75
A$_5$	12.12	15.61	4.64	−1.96
A$_6$	11.75	15.28	6.04	−0.76
A$_7$	14.32	15.11	−0.60	1.31
PAN	10.87	16.24	10.30	−1.31
PMMA	9.37	—	12.68	—

Table III Intramolecular Expansion Factors and θ Solvent Compositions

Sample No.	Composition of θ Solvent		$\|\eta\|_\theta$ at 30°C (dL/g)	$\|\eta\|$ in DMF at 30°C (dL/g)	Intramolecular Expansion Factor (α)
	DMF (%)	Methanol (%)			
A_1	34.0	66.0	0.16	0.38	1.334
A_2	33.2	66.8	0.13	0.30	1.321
A_3	40.0	60.0	0.13	0.31	1.336
A_4	38.0	62.0	0.17	0.30	1.208
A_5	61.2	38.8	0.21	0.58	1.403
A_6	60.0	40.0	0.23	0.66	1.421
A_7	58.4	41.6	0.39	1.16	1.438
PMMA	30.0	70.0	0.08	0.35	1.636
PAN	77.2	22.8	0.15	1.16	1.978

Figure 4 and results are given in Table IV. It was observed that value of ν for all systems at all temperatures remains constant at 2.5 ± 0.0052 for 42 determinations. The r.s.d. was found to be 0.2%. This indicates that in the concentration range studied the copolymer molecules are spherical in the solution,[15] whereas for oblates or prolates, it is reported that ν values differ widely from 2.5.[16,17]

Swelling Behavior

From the results of the swelling of random copolymers (Fig. 5), it is observed that % swelling increases in water with the increase of AN content in the copolymer, whereas it goes on decreasing with other less polar solvents like methanol, absolute alcohol,

1-propanol, and cyclohexane. Because of the hydrogen-bonding character of water as well as PAN, the swelling extent increases with increasing AN concentration in the copolymer. It has also been observed that for a particular sample of copolymer the percent swelling goes on decreasing in methanol, absolute alcohol, 1-propanol, and cyclohexane. This may be due to the decreasing order of polarity (hydrophilicity) of these solvents. Copolymers with polar CN groups allow the polar solvent to penetrate into it. Hence, penetration of solvent molecules into polymer molecules increases with increasing polarity of the solvent, which results in increased swelling. It has also been observed that though water is the most polar solvent among the five solvents used, the copolymers do not show maximum swelling in water.
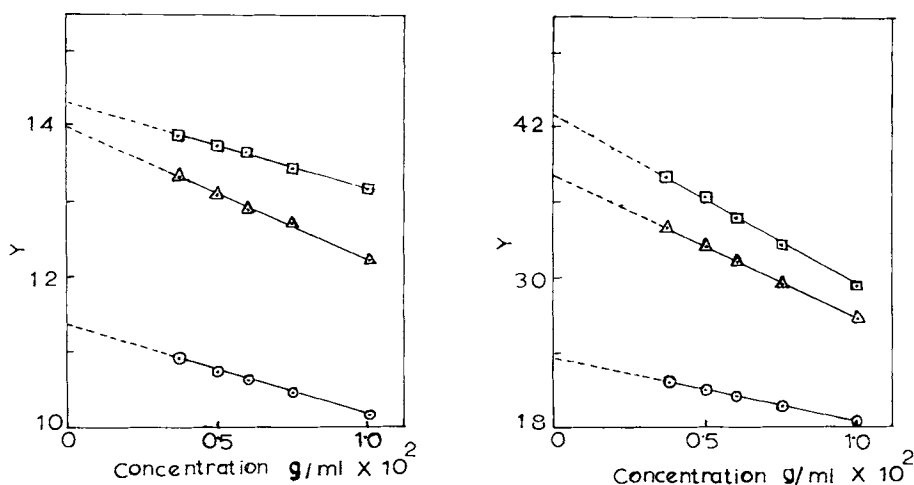
Figure 4 Plot of Y against concentration g/cm^3 where $Y = (\eta_r^{0.5} - 1)/[C(1.35\ \eta_r^{0.5} - 0.1)]$. (a) in DMF: ($\triangle$) A_1 at 40°C; ($\odot$) A_2 at 40°C; ($\square$) PMMA at 30°C; (b) in DMSO; ($\odot$) A_6 at 30°C; ($\triangle$) A_7 at 50°C; ($\square$) PAN at 30°C.

Table IV Hydrodynamic Volumes of Polymers in DMF and DMSO

| Sample No. | V_emL/g | | | | | |
| | In DMF | | | In DMSO | | |
	30°C	40°C	50°C	30°C	40°C	50°C
A_1	15.20	14.00	13.07	12.71	11.84	11.73
A_2	11.95	11.37	11.39	10.46	10.06	10.41
A_3	12.52	12.19	12.00	12.38	12.25	11.79
A_4	11.86	10.27	10.02	12.04	11.59	11.36
A_5	23.20	22.03	20.00	23.10	22.92	21.88
A_6	26.13	25.24	22.12	24.26	24.26	23.64
A_7	46.22	40.00	36.50	40.80	40.70	39.74

This may be due to the unmatching solubility parameter [47.86×10^3 $(J/m^3)^{1/2}$ for water] of the copolymer. The solubility parameter of a randomly chosen MMA : AN (2 : 3 v/v) sample was determined by plotting the intrinsic viscosity against the solubility parameters of the solvents. Six fractions of the 2 : 3 v/v (MMA : AN) copolymer were collected by precipitating the copolymer from its 2%
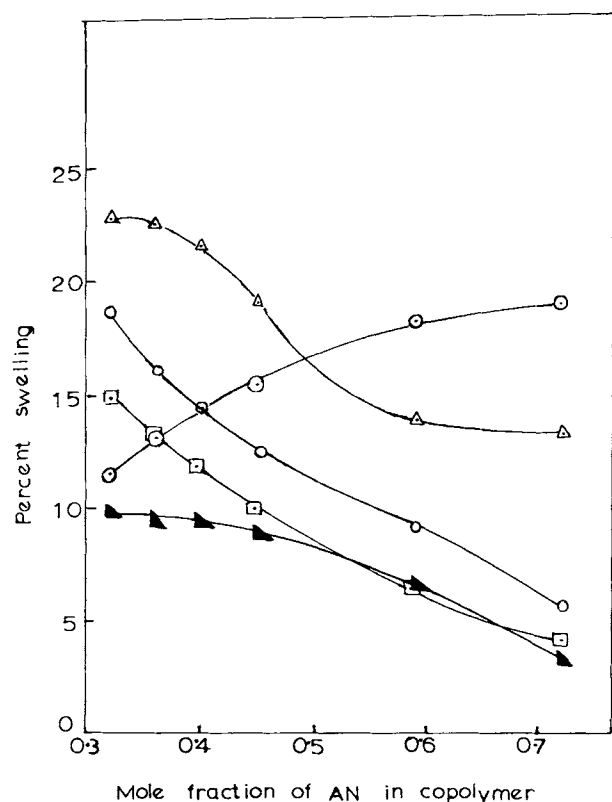

Figure 5 Swelling behavior of copolymers in solvents: (○) water; (△) methanol; (▲) cyclohexane; (▢) 1-propanol; (○) absolute alcohol.

solution in DMF by successive addition of methanol. Intrinsic viscosities of each fraction were determined in different solvents: benzene, chlorobenzene, 1,4-dioxane, acetic anhydride, diethylformamide, and dimethylacetamide. The solubility parameter of the copolymer was calculated from the plot of intrinsic viscosity against the solubility parameter of the solvent, assuming that the intrinsic viscosity of the copolymer attains maximum value when the solubility parameter of the copolymer falls in the vicinity of that of the solvent δp. The solubility parameter of the copolymer has been estimated by equating it to that of the solvent at which intrinsic viscosity has the maximum value in the plot of $|\eta|$ against δ. It was observed that all six fractions of the copolymer 2 : 3 (v/v) MMA : AN showed a 20.4×10^3 $(J/m^3)^{1/2}$ solubility parameter, which lies in between 19×10^3 and 30.68×10^3 $(J/m^3)^{1/2}$ values reported for PMMA and PAN, respectively.[18,19]

Measurements of dn/dc

The dn/dc values of MMA–AN copolymers and PAN and PMMA were calculated at 632.8 nm. The dn/dc values in DMF showed very little dependence on copolymer concentration in solution. The dn/dc values calculated (by assuming that the individual components of the copolymer contributes to the dn/dc in proportion to their known weight fractions) along with observed values are given in Table V. The theoretical values of dn/dc were calculated as

$$\nu' \text{ copolymer} = dn/dc = W_A\nu'_A + W_B\nu'_B$$

where ν'_A and ν'_B are the specific refractive index increments of components A and B of the copolymer and W_A and W_B are their corresponding weight

Table V   Differential Refractometric Analysis (Cell Constant 0.0008)

Sample No.	Weight Fraction of AN	Weight Fraction of MMA	dn/dc	
			Calculated	Observed
A_1	0.202	0.798	0.061	0.081
A_2	0.227	0.773	0.062	0.046
A_4	0.299	0.701	0.065	0.076
A_5	0.437	0.563	0.070	0.093
A_6	0.466	0.534	0.071	0.068
A_7	0.578	0.422	0.076	0.059
PAN	—	—	0.081 (Reported)	0.092
PMMA	—	—	0.055 (Reported)	0.053

fractions. The weight fraction values were obtained by gravimetric analysis of nitrogen, and v'_A and v'_B were determined experimently for homopolymers PAN and PMMA. It was observed that experimental values show 25% deviation from the calculated values except for the copolymers where MMA:AN composition is 1 : 2 (A6 sample), and these results indicate that only weight fractions of the individual components are not contributing toward the dn/dc values, but the morphological arrangements of the components in the copolymer are equally responsible for the dn/dc values. In the present study, with the copolymers being random in nature, an $\sim$ 25% deviation in values from the ideal behavior is observed, indicating that the randomness or disorder in copolymer conformation is within 25%.

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