

Temperature Influence on the Heterocontact Interactions in Styrene-Acrylonitrile Copolymers

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The influence of temperature on the heterocontact interactions of styrene-acrylonitrile copolymers in dimethylformamide and γ -butyrolactone has been studied. The values of K_0 (Flory constant related to unperturbed dimensions) have been determined by the Stockmayer-Fixman and Inagaki-Ptitsyn equations. The average mean square unperturbed end-to-end dimensions decrease with increase in temperature, indicating a reduction in skeletal chain dimensions due to decrease of heterocontact interactions with increase in temperature. Although there is slight temperature effect on the heterocontact interactions, it is masked by the deswelling of the copolymer chain with rise in temperature.

HETEROCONTACTS in a nonpolar binary random copolymer brings about changes in short range and long range interactions in solution, resulting in an expansion of the chain dimensions. The expansion is high in comparison to that of parent homopolymers¹.

In the case of homopolymers the short range and long range interactions change with increase in temperature due to changes in steric hindrance and solute-solvent interactions respectively². But for copolymers an additional change takes place in the short and long range interactions with increase in temperature due to heterocontact interactions.

Dondos and Benoit³ showed that as the temperature is increased the unperturbed dimensions approach the ideal value. If the unperturbed average dimensions of a copolymer chain conforms to an idealized random flight model and consists of two different kinds of independent statistical chain elements, the unperturbed mean square end-to-end distance $\langle r_0^2 \rangle$ obeys the relation

$$\left(\frac{\overline{r_0^2}}{\overline{M}_w}\right)_{CO} = W_A \left(\frac{\overline{r_0^2}}{\overline{M}_w}\right)_A + W_B \left(\frac{\overline{r_0^2}}{\overline{M}_w}\right)_B \quad \dots(1)$$

where W_A and W_B are the weight fractions and the quantities in parenthesis are characteristics of homopolymers.

According to Dondos and Benoit, the excess interaction parameter χ_{AB} decreases and ultimately approaches zero with increase in temperature. These two manifestations indicate that the heterocontact interactions are temperature dependent and could be eliminated at an appropriate temperature. However, this generalization is yet to be substantiated with experimental evidence.

In this paper, a critical analysis of the effect of temperature on the heterocontact interactions of styrene-acrylonitrile (St-AN) copolymers in solution is presented.

Materials and Methods

St-AN copolymers (SA1, 0.274 mole fr. of AN, SA2, 0.385 mf of AN and SA3, 0.475 mf of AN) were prepared by free radical polymerization. Experimental conditions employed for copolymerization, fractionation of the copolymers and the determination of weight average molecular weights (\overline{M}_w) by light-scattering method have been presented in a previous paper⁴.

The values of limiting viscosity number $[\eta]$, evaluated at 30°, 40°, 50° and 60° \pm 0.05° in DMF and γ -butyrolactone are given in earlier publication⁵.

Results and Discussion

The dependence of limiting viscosity number $[\eta]$ on molecular weight in a good solvent (i.e. in a non-ideal system), is an useful approach to evaluate unperturbed chain dimensions, i.e. short range interactions such as K_0 or $\langle r_0^2 \rangle$ and the long range solute-solvent interactions parameter B .

A number of graphical procedures have been proposed to evaluate these parameters in recent times from $[\eta]$ in a non-ideal solvent⁷⁻¹². These methods are based on the relation of $\alpha\eta$ with Z, α_η being the hydrodynamic expansion factor and

$$Z = (3/2\pi)^{3/2} (B/A^3) M^{1/2} \quad \dots(2)$$

where $B = (\beta/m_s^2)$ and $A = [\langle r_0^2 \rangle / M]^{1/2} = l^2/6m_s$, where A and B represent the short range and long range interactions respectively, M is the molecular weight of the polymer, l^2 and m_s are the mean square length and molar weight of a segment of the statistical model, β is the binary cluster integral between any pair of segments which vanishes as T approaches θ (the theta temperature).

The relative merits of graphical procedures have been discussed at length by a number of workers^{11,12}. In the present case, Stockmayer-Fixman (SF) and Inagaki-Ptitsyn (IP) equations were used to evaluate K_0 ; and B values. Details of the evaluations

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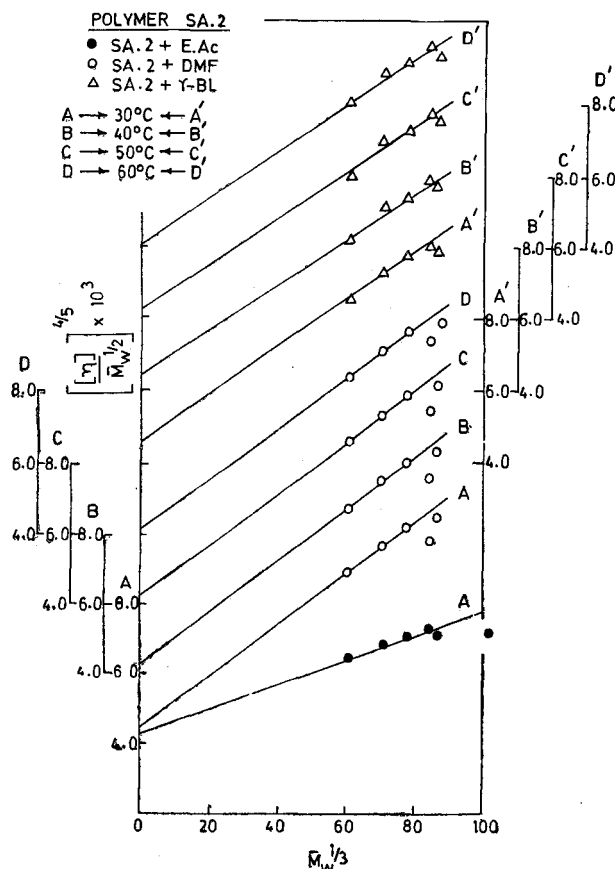


Fig. 1 — Plots of Inagaki-Ptitsyn equation for the evaluation of K_0 for copolymer SA2 in different solvents

are given in an earlier communication¹³. Figs. 1 and 2 give the specimen plots of SF and IP equations for the copolymer SA2, in DMF and γ -BL at different temperatures along with the plot in ethyl acetate (EtAc) at 30°. Table 1 gives the K_0 values obtained; K_0 values for polystyrene (PSt) in both the solvents are also included.

Specific solvent effect is negligible on K_0 values for all the three copolymers. Skeletal chain dimensions are slightly diminished with increase in temperature. K_0 values are different in both the methods except in few cases and are increased with increase in AN content.

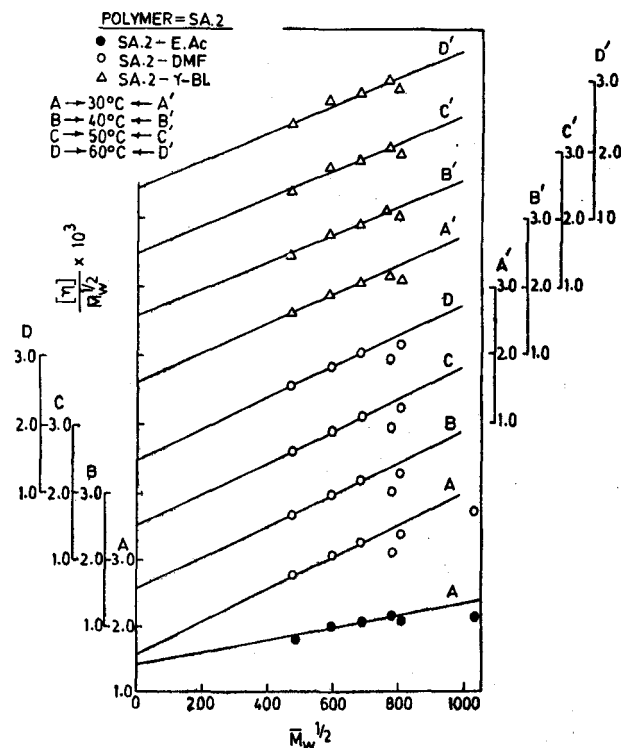


Fig. 2 — Plots of Stockmayer-Fixman equation for the evaluation of K_0 for copolymer SA2 in different solvents

K_0 values are independent of temperature for PAN in DMF¹⁴ and decrease with increase in temperature for PSt in DMF and γ -BL^{15,16}. In the case of acrylonitrile-methylacrylate copolymer in DMF, K_0 values are independent of temperature¹⁷. In the present case it is difficult to assume that the change in K_0 values is negligible in the light of errors involved in the measurement of $[\eta]$ and M_w , because for a given temperature in the two solvents K_0 values are almost identical. It is, therefore, possible to predict that a reduction in the unperturbed chain dimensions is taking place with increase in temperature.

Average mean square unperturbed end-to-end dimensions were calculated from the values of K_0 obtained from SF equation. The values are given in Table 2.

TABLE 1 — VALUES OF K_0 FROM DIFFERENT METHODS

Polymer	Method	$K_0 \times 10^3$								
		In DMF				In γ -BL				In EtAc 30°
		30°	40°	50°	60°	30°	40°	50°	60°	
SA1	SF	0.96	0.95	0.94	0.93	0.98	0.95	0.93	0.90	0.96
	IP	0.89	0.83	0.81	0.78	0.86	0.82	0.80	0.78	0.95
SA2	SF	1.61	1.57	1.53	1.49	1.60	1.56	1.50	1.48	1.43
	IP	1.58	1.50	1.43	1.42	1.59	1.51	1.45	1.38	1.48
SA3	SF	1.73	1.73	1.69	1.66	1.62	1.57	1.50	1.43	1.63 ^a
	IP	1.62	1.58	1.48	1.42	1.59	1.55	1.50	1.41	1.58 ^a
PSt ¹⁵	SF	0.85	0.82	0.78	0.72	0.82	0.79	0.76	0.73	0.84
PAN		Unaffected with temperature								

(a) Values in MEK.

The mean square end-to-end distances $\langle \bar{r}_0^2 \rangle / \bar{M}_w$ for an idealized random flight chain, were calculated by Eq. (1) and these values are 5.18×10^{-17} , 5.49×10^{-17} , 5.79×10^{-17} for SA1, SA2 and SA3 respectively. $\langle \bar{r}_0^2 \rangle / \bar{M}_w$ values, obtained experimentally, are high for SA2 and SA3 while for SA1, they are nearly identical. High values of $\langle \bar{r}_0^2 \rangle / \bar{M}_w$ indicate the presence of heterocontact interactions. The decrease in these values with increase in temperature, may be interpreted as due to decrease in the skeletal chain dimensions or due to the reduction of the heterocontact interactions with temperature.

Unperturbed chain dimensions are independent of temperature for PAN in DMF while for PSt they are reduced relatively in DMF and in γ -BL. The order of reduction is identical for PSt and for the copolymers. It is, therefore, possible to predict that the reduction in the chain dimensions are due to the reduction in the steric hindrance as in the case of PSt in both the solvents. It is also possible to predict that the heterocontacts are not influenced by the temperature.

Long range interactions—The long range interaction parameter B , which is directly connected to $(\frac{1}{2} - \chi_1)^{18}$, was evaluated from the slopes of SF and IP equations (Figs. 1 and 2) and the values are given in Table 3.

TABLE 2 — VALUES OF UNPERTURBED CHAIN DIMENSIONS FOR COPOLYMERS

Polymer	Temp. °C	$\left[\frac{\langle \bar{r}_c^2 \rangle}{\bar{M}_w} \right] \times 10^{17}$	
		(cm ²)	
		DMF	γ -BL
SA1	30	5.04	5.10
	40	4.99	5.01
	50	4.96	4.92
	60	4.92	4.83
SA2	30	7.12	7.09
	40	7.00	6.97
	50	6.88	6.79
	60	6.76	6.72
SA3	30	7.47	7.15
	40	7.47	7.00
	50	7.36	6.79
	60	7.27	6.58

B values obtained by both the equations are different, and decrease with increase in temperature. The order of decrease in both the methods are identical.

In order to understand the influence of temperature on the heterocontact interactions, χ_1 (the solute-solvent interaction parameter of the copolymer) is calculated from the values of B . χ_1 is related to the extra interaction parameter χ_{AB} through the mole fraction of the two constituent monomers by Eq. (3).

$$\chi_1 = \chi_A \chi_A + \chi_B \chi_B - \chi_A \chi_B \chi_{AB} \quad \dots(3)$$

where χ_A and χ_B are the interaction parameters of the parent homopolymers and χ_A and χ_B are the mole fractions. χ_1 values, evaluated for the three copolymers and for PSt in DMF, and γ -BL are given in Table 4. χ_1 values for PAN taken from literature¹⁹ are also included in Table 4.

For a binary copolymer of nonpolar monomers, χ_1 will be smaller and the solvent therefore 'better' when χ_{AB} will be positive. In the present case, χ_1 values are comparatively high for all the copolymers

 TABLE 4 — VALUES OF χ_1 FOR THE COPOLYMERS

Polymer	Temp. °C	χ_1 in	
		DMF	γ -BL
SA1	30	0.444	0.450
	40	0.446	0.453
	50	0.448	0.454
	60	0.450	0.456
SA2	30	0.449	0.455
	40	0.450	0.457
	50	0.451	0.459
	60	0.453	0.459
SA3	30	0.439	0.446
	40	0.444	0.447
	50	0.445	0.447
	60	0.447	0.478
PSt ¹⁶	30	0.486	0.494
	40	0.486	0.493
	50	0.486	0.493
	60	0.486	0.493
PAN ¹⁴	20	0.280	0.338
	35	0.291	0.330
	50	0.295	0.335
	60	0.295	0.344

 TABLE 3 — VALUES OF $(B \times 10^{27})$ FOR THE COPOLYMERS

Method	Temp. °C	SA1		SA2		SA3	
		DMF	γ -BL	DMF	γ -BL	DMF	γ -BL
SF	30°	2.00	1.72	1.76	1.56	2.06	1.85
	40°	1.93	1.67	1.73	1.48	1.90	1.81
	50	1.86	1.64	1.68	1.43	1.88	1.79
	60	1.78	1.58	1.61	1.40	1.81	1.78
IP	30	3.21	2.90	2.60	2.13	3.16	2.63
	40	3.27	2.81	2.46	2.06	3.08	2.51
	50	3.27	2.76	2.53	2.09	3.04	2.54
	60	3.17	2.67	2.37	2.14	2.99	2.56

and are observed to increase with increase in temperature. χ_1 is practically independent of temperature for PSt in both the solvents while for PAN, χ_1 increases with increase in temperature and values are quite small.

The increase in χ_1 indicates decrease in the solvent power and hence the decrease in the chain extension with rise in temperature. In the case of PAN, the increase in χ_1 is explained as due to the deswelling of the polymer chain in solution^{2,14,17}. The influence of temperature on the long range interactions of PSt in these two solvents is negligible. It is, therefore, possible to assume that the AN sequences in the polymer chain are influenced by the temperature and the increase is due to the deswelling of these units in solution.

The same trend is noticed in the case of acrylonitrile-methyl-acrylate copolymers in DMF¹⁷. In this case increase in χ_1 is attributed to changes in polymer-solvent interactions rather than in chain stiffness. It can be assumed that similar changes are taking place in the St-AN copolymer systems also.

It can thus be concluded that the influence of temperature on heterocontact interaction is negligible and if it exists it is difficult to evaluate. χ_{AB} values from the Eq. (3) are negative and negative χ_{AB} values are difficult to explain at this stage.

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