

## Dilute Solution Properties of Styrene-Acrylonitrile Random Copolymers: Part III—Temperature Variation of Limiting Viscosity Number

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Received 24 May 1976; accepted 18 November 1976

Viscosity measurements for styrene-acrylonitrile random copolymers (St-AN) have been carried out at 30°, 40°, 50°, and 60° ± 0.05° in dimethylformamide (DMF) and  $\gamma$ -butyrolactone ( $\gamma$ -BL). Log $[\eta]$  versus log  $M_w$  (Mark-Houwink relation) relation is established in both the solvents at four temperatures. It is found that the exponent  $a$ , of M-H equation increases with increase in temperature, analogous to that of parent homopolymers, indicating that the chains are in an extended conformation. Limiting viscosity number  $[\eta]$  is found to decrease with increase in temperature. The negative temperature coefficient of  $[\eta]$  has been analysed and  $d \ln [\eta]/dt$  calculated. The value is negative and found to be almost the same for all the samples thus indicating that the composition of AN has no effect on these values.

**E**XPERIMENTAL data of styrene-acrylonitrile (St-AN) random copolymers in different solvents were discussed by two-parameter theory<sup>1,2</sup>. From the long-range interactions, the excess interaction parameter  $\chi_{AB}$  or  $\Delta B_{AB}$  was also evaluated. In this paper the influence of temperature on limiting viscosity number  $[\eta]$  is presented.

### Materials and Methods

St-AN copolymers (SA1, 0.274 mf, of AN; SA2, 0.385 mf of AN; and SA3, 0.475 mf of AN)

were prepared by free radical initiation and the experimental conditions employed for copolymerization, fractionation and the determination of weight average molecular weight by light-scattering method have been presented in an earlier paper<sup>1</sup>.

The values of limiting viscosity number  $[\eta]$  were estimated at 30°, 40°, 50° and 60° ± 0.05° in DMF (dimethyl formamide) and  $\gamma$ -BL ( $\gamma$ -butyrolactone). Table 1 gives the values of  $[\eta]$  for all the copolymers at the respective temperatures.

TABLE 1 — VALUES OF  $[\eta]$  (dl/g) FOR ALL THE COPOLYMERS AT DIFFERENT TEMPERATURES

Fr. No.	$M_w \times 10^{-5}$	$[\eta]$ in DMF				$[\eta]$ in $\gamma$ -BL			
		30°	40°	50°	60°	30°	40°	50°	60°
POLYMER SA1									
SA 11	5.768	1.960	1.930	1.898	1.870	1.875	1.820	1.755	1.705
SA 12	3.788	1.545	1.550	1.493	1.480	1.478	1.452	1.422	1.388
SA 14	2.963	1.333	1.310	1.281	1.248	1.235	1.190	1.150	1.130
SA 15	2.479	1.140	—	—	—	—	—	—	—
SA 16	2.091	1.021	0.990	0.982	0.940	0.943	0.925	0.905	0.890
SA 17	1.435	0.753	0.735	0.723	0.713	0.713	0.698	0.675	0.648
SA 18	0.7305	0.460	0.448	0.437	0.425	0.430	0.415	0.400	0.3965
POLYMER SA2									
SA 21	10.600	3.815	—	—	—	—	—	—	—
SA 22	6.470	2.722	2.644	2.590	2.510	2.495	2.430	2.370	2.305
SA 23	6.013	2.410	2.330	2.295	2.270	2.445	2.390	2.340	2.310
SA 24	4.718	2.227	2.185	2.140	2.068	2.095	2.000	1.955	1.920
SA 25	3.522	1.797	1.759	1.713	1.662	1.712	1.670	1.640	1.610
SA 27	2.248	1.300	1.273	1.243	1.208	1.228	1.170	1.120	1.100
POLYMER SA3									
SA 32	7.776	3.650	3.550	3.495	3.350	3.275	3.203	3.105	3.020
SA 34	7.161	3.420	3.370	3.290	3.195	3.180	3.107	3.020	2.930
SA 35	5.350	2.730	2.662	2.597	2.540	2.535	2.475	2.448	2.382
SA 36	3.733	2.110	2.057	2.000	1.955	1.935	1.870	—	1.770
SA 37	2.575	1.620	1.580	1.550	1.500	1.513	1.494	1.824	1.450
SA 38	1.400	1.038	1.022	0.990	0.9525	0.959	0.934	0.910	0.875

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Results and Discussion

**Mark-Houwink relation** — From the plots of  $\log [\eta]$  versus  $\log \bar{M}_w$  (Fig. 1) at the temperatures studied, Mark-Houwink (M-H) relation was established for St-AN copolymers. The values of  $K'$  and  $a$  are given in Table 2, along with the values of  $K'$  and  $a$  for polystyrene (PSt).

The exponent  $a$  of the M-H relation increases almost linearly with temperature for St-AN copolymers in the solvents studied, thus indicating that the chain extension is larger, the higher the temperature.

The chain extension in the case of copolymers is due to two factors: (i) the excluded volume effect and (ii) the repulsive nature of unlike monomer unit interactions (i.e.  $A$ - $B$  type of interactions).

The repulsive ( $A$ - $B$ ) interactions decrease with increase in temperature<sup>3</sup>, as a result of which the chain extension may decrease. On the other hand, there is a chain extension<sup>4</sup> with an increase in temperature due to excluded volume effect. If both of these effects oppose each other the net effect would be due to the factors which predominate.

The values of  $a$  for polyacrylonitrile (PAN) and PSt in DMF and in  $\gamma$ -BL is found to increase with increase in temperature<sup>5-7</sup>, similar to the values of  $a$  in the case of copolymers SA1, SA2 and SA3 in DMF and in  $\gamma$ -BL (values of  $a$  for PAN varied from 0.73 to 0.77 in  $\gamma$ -BL, 0.745 to 0.76 in DMF. These values are taken from ref. 5).

It is therefore, difficult at this stage to predict which factor, i.e. either factor (i) or factor (ii) is responsible for the extension of the copolymer chain in solution.

**Temperature variation of  $[\eta]$**  — The plots of limiting viscosity number  $[\eta]$  versus temperature are linear in the case of SA1, SA2 and SA3 and the slopes are negative in all the cases and in both the solvents (Fig. 2).

The variation of  $[\eta]$  with temperature in polymer solutions has been studied extensively. The negative temperature coefficient of  $[\eta]$  is explained by the decrease of  $A$  (i.e. the short-range interaction parameter) rather than the increase in  $B$  (i.e. long-range interaction parameter) with temperature. It was pointed out<sup>8</sup> that the chains are most expanded at the temperature at which  $[\eta]$  is maximum. The decrease of  $[\eta]$ , afterwards, is due to the decrease in the value of  $A$ .

In the case of stiff polymers, such as cellulose derivatives, the negative temperature coefficient is mainly attributed to the rapid decrease of  $A$ ,

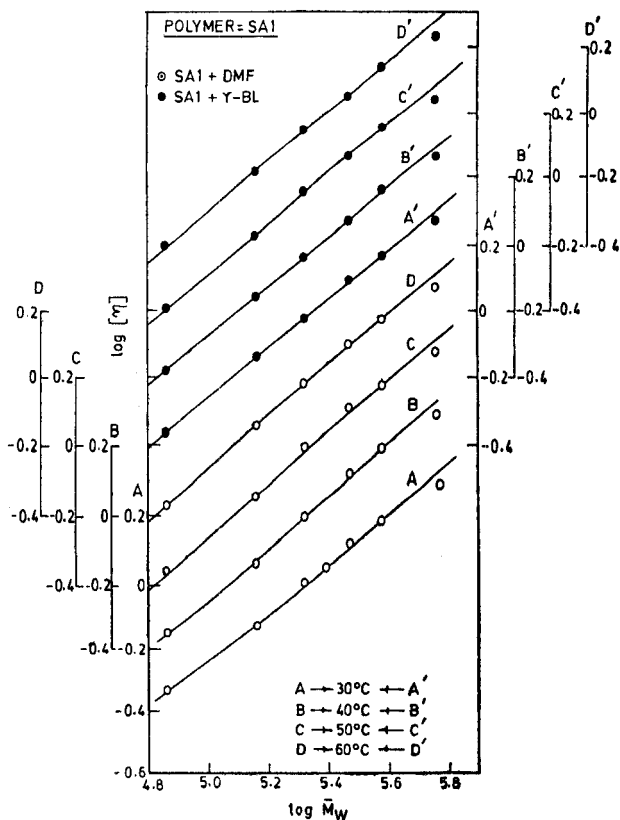


Fig. 1 — Mark-Houwink relationship for the polymer SA1

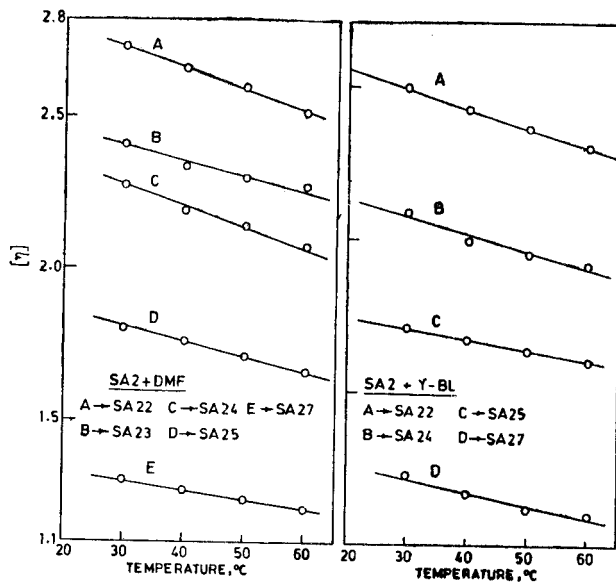


Fig. 2 — Temperature variation of  $[\eta]$  for the polymer SA2 in DMF and  $\gamma$ -butyrolactone ( $\gamma$ -BL)

TABLE 2 — VALUES OF  $K'$  AND  $a$  OF COPOLYMERS AT DIFFERENT TEMPERATURES

Polymer	Solvent	$a$ at				$K' \times 10^4$ at			
		30°	40°	50°	60°	30°	40°	50°	60°
SA1	DMF	0.74	0.75	0.76	0.77	1.20	1.01	0.84	0.74
	$\gamma$ -BL	0.73	0.74	0.76	0.77	1.24	1.08	0.83	0.73
SA2	DMF	0.73	0.74	0.75	0.76	1.62	1.39	1.19	1.02
	$\gamma$ -BL	0.72	0.73	0.74	0.75	1.75	1.43	1.20	1.07
SA3	DMF	0.73	0.74	0.745	0.75	1.72	1.60	1.42	1.28
	$\gamma$ -BL	0.725	0.73	0.74	0.75	1.78	1.59	1.44	1.27
PSt	DMF	0.688	0.697	0.716	0.728	1.05	0.94	0.71	0.59
	$\gamma$ -BL	0.632	0.640	0.660	0.692	1.67	1.49	1.15	0.74

TABLE 3 — VALUES OF  $d \ln [\eta]/dT$  FOR THE COPOLYMERS

Solvent	$d \ln [\eta]/dT \times 10^3$				
	SA1	SA2	SA3	PAN	PSt
DMF	-2.2	-2.5	-2.6	-1.9 <sup>6</sup>	-1.11 <sup>6</sup>
$\gamma$ -BL	-2.5	-2.5	-2.6	-2.88 <sup>6</sup>	-1.85 <sup>7</sup>

rather than changes in  $\alpha_n^3$  (i.e. the viscosity expansion factor). But the negative temperature coefficient in the case of PAN was mainly attributed as entropic in origin<sup>5-12</sup>.

The negative temperature variation of limiting viscosity number can best be understood if the relative contribution of short-range and long-range interactions to  $[\eta]$  is separated. The separation can be obtained as follows<sup>4</sup>:

$$[\eta] = K_0 M^{1/2} \alpha_n^3 \quad \dots(1)$$

since

$$K_0 = \phi_0 \left[ \frac{\langle \bar{r}_0^2 \rangle}{M} \right]^{3/2}$$

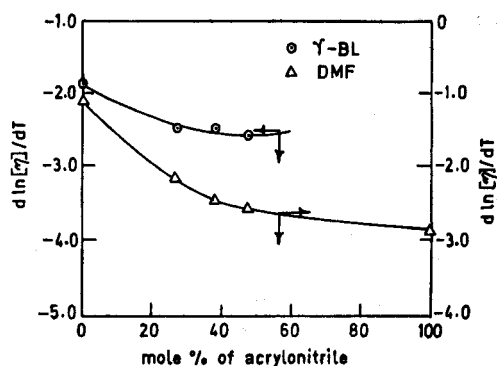
where  $\langle \bar{r}_0^2 \rangle$  is the unperturbed mean square end-to-end distance. Eq. (1) can be written as

$$\frac{d \ln [\eta]}{dT} = \frac{3}{2} \frac{d \ln \langle \bar{r}_0^2 \rangle}{dT} + \frac{3 d \ln \alpha_n}{dT} \quad \dots(2)$$

Thus the  $d \ln [\eta]/dT$  is controlled by the sum of the two factors: the first one represents the short-range interaction and the second one the long-range interactions.

The values of  $d \ln [\eta]/dT$  are calculated for the fractions of SA1, SA2 and SA3 in DMF and  $\gamma$ -BL and for PSt in  $\gamma$ -BL. The average values are given in Table 3.

The values of  $d \ln [\eta]/dT$  in both the solvents are almost identical except in the case of SA1 where the values in DMF are slightly higher than those in  $\gamma$ -BL. The values of  $d \ln [\eta]/dT$  for PAN in  $\gamma$ -BL is not available, but it is known that the temperature coefficient of  $[\eta]$  of PAN in  $\gamma$ -BL is negative<sup>5</sup>.  $d \ln [\eta]/dT$  for PSt calculated (Table 3) is also negative. It is interesting to note that the values of  $d \ln [\eta]/dT$  of the three copolymers St-AN in both the solvents are negative and closely analogous to those of homo polymers. Fig. 3 gives


 Fig. 3 — Plots of  $d \ln [\eta]/dT$  versus mole % of acrylonitrile

the  $d \ln [\eta]/dT$  versus mole % of AN in the copolymer.

An evaluation of  $d \ln [\eta]/dT$  from the contributions of short-range and long-range interactions needs independent evaluation of two factors of the right-hand side of Eq. (2). It is difficult at present to evaluate these contributions in order to verify the values of  $d \ln [\eta]/dT$  as it needs additional experimental data.

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