

**Viscometric Studies:  
Interpolymer Complex Formation Between  
Poly(Styrene-b-Ethylene Oxide)  
Block Copolymers and Poly(Acrylic Acid)**

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SUMMARY

Interpolymer complex formation between poly(styrene-b-ethylene oxide) block copolymers (PS-PEO) and poly(acrylic acid) (PAA) has been studied by viscometry using THF-water mixture of several compositions as solvent.

Unlike alternating and random copolymers, composition of the complex formed between (PS-PEO) and PAA does not seem to be affected by the molecular characteristics of the copolymer and the solvent composition. However the nature of the reduced viscosity curves during complex formation was found to be dependent on solvent composition and this has been interpreted in terms of preferential solvation, conformation and micellization of the block copolymer molecules.

INTRODUCTION

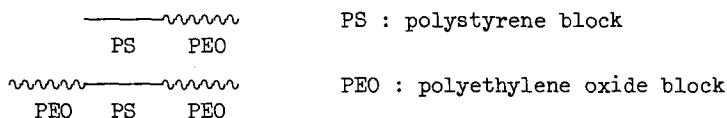
Interaction between macromolecules may lead to the formation of interpolymer complexes, which have already found applications in technology, medicine and other fields (BEKTUROV and BIMENDINA 1981). However, most of the studies on this subject have been confined on the interactions between homopolymers (OHNO et al 1978 ; IKAWA et al 1975 ; OHNO et al 1980). The properties of a series of complexes between alternating, and random copolymers with nonionic polymers have also been reported in the literature (BIMENDINA et al 1977 ; BIMENDINA 1979 ; BEKTUROV et al 1979 ; TLEUBAEVA et al 1979 ; SALTIBAEVA et al 1979). Composition of these complexes were found to be different from that obtained in case of homopolymers. This discrepancy has been attributed to the increase in distance between active groups in the copolymer and the steric hindrance caused by the bulky functional groups (BEKTUROV and BIMENDINA 1981). Both these difficulties could be circumvented in the case of block copolymers.

Poly(styrene-b-ethylene oxide) block copolymers (PS-PEO) have been chosen for the present investigation because of two main reasons, e.g. (i) one can obtain well defined structures, molecular weights and compositions for these copolymers, (ii) PEO homopolymer is known to form a stable complex with poly(acrylic acid) (PAA). It would also be of interest to find out whether conformation of the copolymer molecules, due to incompatibility of the dissimilar blocks present in them, or micelle formation, could affect complex formation with PAA. Attempts have been made in this paper to correlate viscometric results in several THF-water mixtures with the composition of the interpolymer complex between PAA and PS-PEO block copolymers of different molecular characteristics.

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EXPERIMENTALSynthesis and characterization of PS-PEO block copolymers

Di- and triblock copolymers have the following structure :



These block copolymers were prepared and characterized according to known techniques (RIESS et al 1977 ; MARTI et al 1975). The molecular characteristics of the copolymers are given in Table 1.

TABLE 1

Sample	Structure	Composition weight % PS	$\bar{M}_n$ PS sequence	$\bar{M}_n$ total
24	triblock	56.3	36,000	64,000
32	diblock	23.2	11,800	50,800
36	diblock	23.8	15,800	65,400
41 A	diblock	15.6	3,700	23,600

Polyacrylic acid (PAA) was supplied by PROTEX in the form of a 25 % aqueous solution. Its molecular weight, determined by viscometry (TAKAHASHI et al 1957) was found to be  $1.03 \cdot 10^5$ .

Solvent. Viscosity and other properties of THF-water mixtures of several compositions have been described elsewhere (CHATTERJEE et al 1982).

Viscosity. The viscosity of the mixed solutions of PAA (1.00 to 1.13 .  $10^{-2}$  unit mol/l) and copolymer at various unit mole ratios of reacting units (ethylene oxide units) was determined at  $25 \pm 0.05^\circ\text{C}$  by an Ubbelohde viscometer for which kinetic energy correction was negligible.

Potentiometric titration. The details of titration procedure have been described elsewhere (CHATTERJEE et al 1982).

RESULTS AND DISCUSSION

Block copolymers are known to exhibit interesting colloidal and interfacial behaviour in the presence of solvents (RIESS et al 1977). It was considered of interest to see how the effect of micellization and preferential solvation of the block copolymers would affect their viscosity behaviour, and whether ultimately they would influence their intrinsic viscosity and ability to form complexes with PAA.

Fig. 1 shows the typical shape of intrinsic viscosity - composition of solvent curve for a PS-PEO block copolymer (sample 41 A).

This curve in fact reflects the micellization at the extreme of the composition of the solvent (TUZAR and KRATOCHVIL 1976). In addition, at the intermediate compositions of the solvent, preferential solvation of the block copolymer does take place as indicated by two distinct maxima, which was also shown by MARTI (1977).

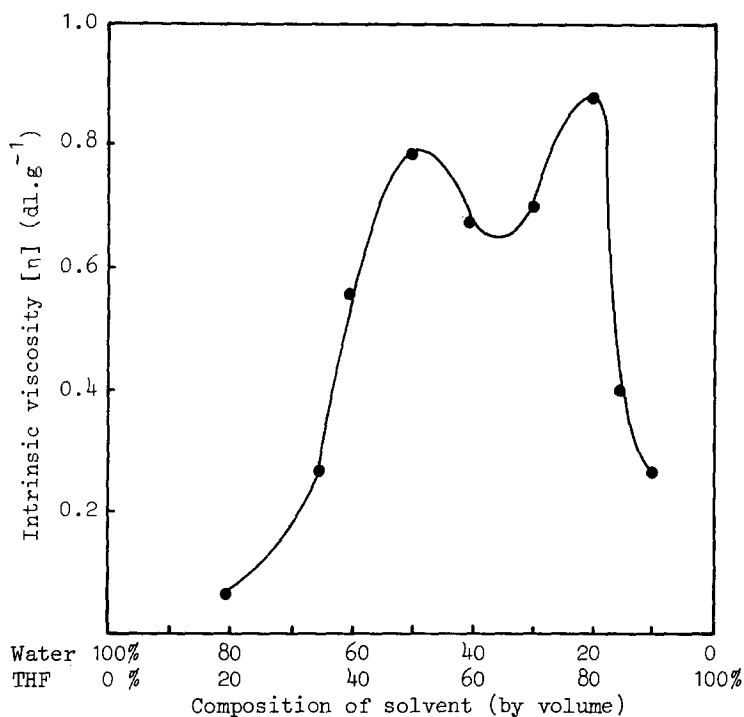


Fig. 1 : Variation of intrinsic viscosity  $[\eta]$  of PS-PEO diblock copolymer (sample 41 A) with the composition of THF-water mixture (composition of solvent by volume percent)

One would expect such variations of intrinsic viscosity of block copolymer solutions because THF and water are good solvents for PS and PEO blocks respectively. Thus, it seemed likely that composition of the solvent is expected to influence the conformation as well as the degree of micellization of the block copolymer.

Fig. 2 and Fig. 3 show the reduced viscosity behaviour of PS-PEO block copolymer (sample 41 A) during its complex formation with PAA. Conventionally, reduced viscosity is calculated with respect to the concentration of PAA ( $C_{PAA}$ ), and unit mole ratio is expressed with respect to the reacting units of the component polymers (BIMENDINA et al 1977).

It can be seen from Fig. 2 and Fig. 3, that irrespective of solvent composition, a distinct break was observed when the unit mole ratio of the reacting units is unity. This, in fact, is a definite indication of interpolymer complex formation as shown previously (OHNO et al 1978 ; OHNO et al 1980). However the nature of the reduced viscosity curves of Fig. 2 and 3 are different and can be classified under two distinct types.

At the intermediate composition of the solvent (e.g. 40 to 80 % THF by volume), the block copolymer molecules are expected to be molecularly dispersed. At this composition region of solvent, reduced viscosity linearly increases till unit mole ratio of reacting units is unity. The rate of increase of reduced viscosity changes beyond this ratio. Similar observations have been made with PEO homopolymers in the same composition range of solvent (CHATTERJEE et al 1982).

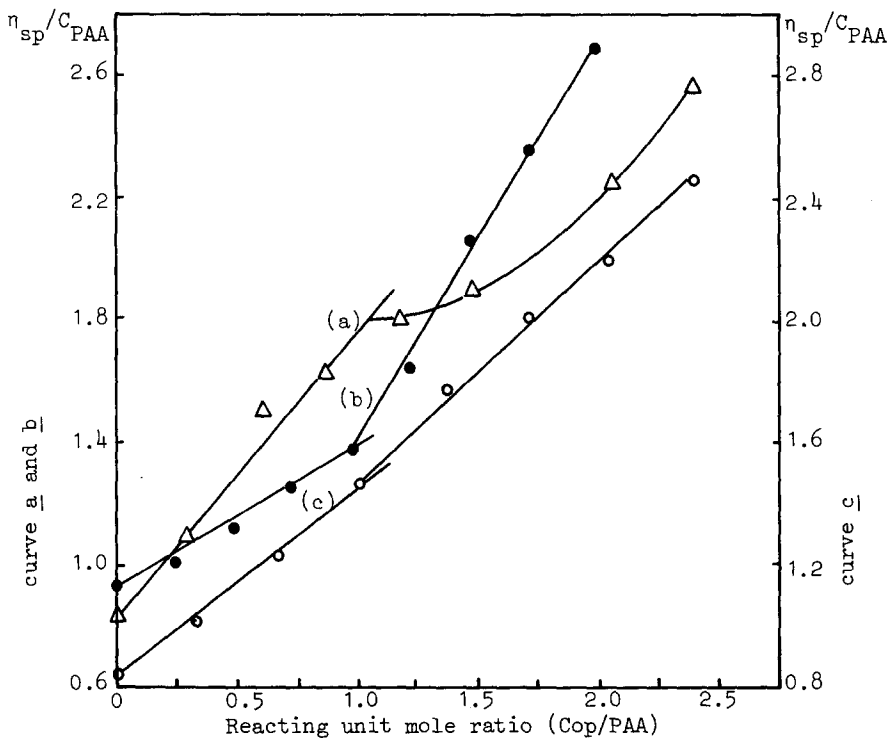


Fig. 2 : Reduced viscosity ( $\eta_{sp}/C_{PAA}$ ) change during complex formation of PS-PEO diblock copolymer (sample 41 A) with PAA in :  
 a) 20 % water + 80 % THF  
 b) 30 % water + 70 % THF  
 c) 50 % water + 50 % THF  
 (Composition of solvent by volume percent)

However it may be mentioned that PAA has a much lower reduced viscosity ( $\eta_{sp}/C_{PAA}$ ) in THF-water mixtures compared to its value in pure water, due to weakening electrostatic repulsion as a result of lower dissociation. The reduced viscosity of PAA does not seem to be very much affected with the composition of the solvent, indicating that PAA molecules acquire a tightly coiled conformation even in the presence of small quantities of THF (CHATTERJEE et al 1982).

Contrary to the behaviour of the extreme composition range of the solvent (e.g. below 40 % THF or above 80 % THF by volume), where the block copolymer molecules are expected to be in the micellar state, a distinct fall in reduced viscosity had been observed till unit mole ratio of reacting units is unity (Fig. 3). This fall may be attributed to different degrees of aggregation and solvation of the interpolymer complex formed between PAA and micellized block copolymer. The increase or constant value of reduced viscosity beyond 1:1 unit mole ratio is obviously related to the low values of intrinsic viscosity of block copolymers in that particular solvent mixture (c.f. Fig. 1) and to the value of reduced viscosity of a 1:1 complex.

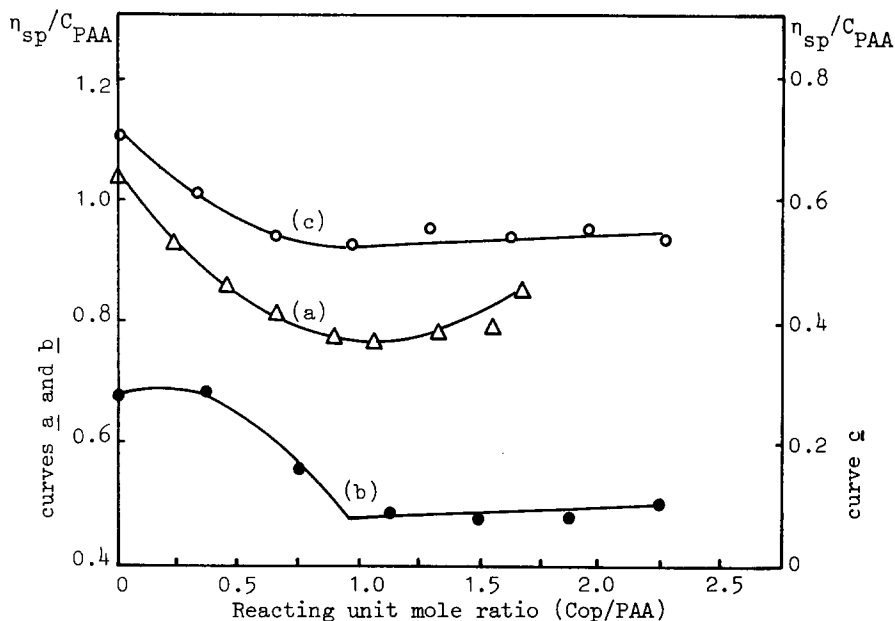


Fig. 3 : Reduced viscosity ( $\eta_{sp}/C_{PAA}$ ) change during complex formation of PS-PEO diblock copolymer (sample 41 A) with PAA in :  
 a) 10 % water + 90 % THF  
 b) 15 % water + 85 % THF  
 c) 70 % water + 30 % THF  
 (Composition of solvent by volume percent)

As shown by earlier workers (OHNO et al 1978, OHNO et al 1980), an additional evidence of interpolymer complex formation could be provided by potentiometric titrations. Fig. 4 shows the apparent pH changes during complex formation between block copolymer and PAA in THF-water mixture of several compositions.

A distinct change in slope appears when the unit mole ratio of reacting units is unity, which is characteristic of interpolymer complex formation.

In order to see the influence of molecular characteristics (e.g. structure, composition and molecular weight) of block copolymers in forming complexes with PAA, other diblock and triblock copolymers have been studied.

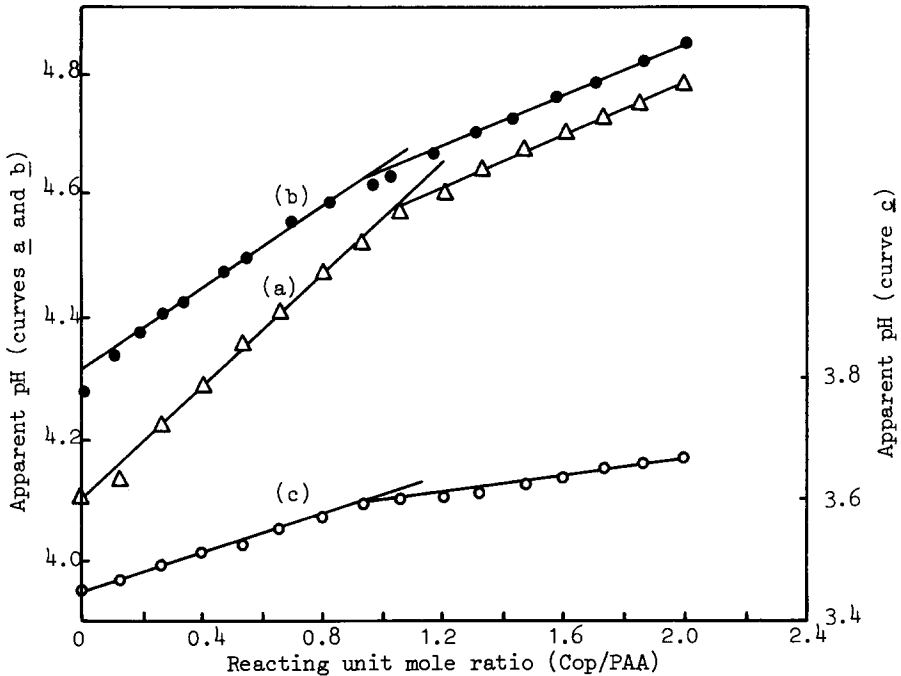


Fig. 4 : Apparent pH change during complex formation between diblock copolymer (sample 41 A) and PAA in :

- a) 10 % water + 90 % THF
- b) 30 % water + 70 % THF
- c) 70 % water + 30 % THF

Fig. 5 shows the reduced viscosity behaviour of block copolymers (samples 24, 32, 36) during complex formation with PAA in 30 % water + 70 % THF (by volume).

On comparing the curves of Fig. 5 with the curve b of Fig. 2, it appears that for the same solvent mixture the nature of the reduced viscosity curve seem to be independant of the molecular characteristics of the copolymer. This obviously indicates that non reacting units (e.g. styrene units of PS sequence) in the copolymer do not interfere in any way with the interaction between active units of the copolymer (e.g. ethylene oxide units of PEO) and PAA. The composition of the interpolymer complex was always found to be 1:1 (unit mole ratio).

Thus we can conclude that unlike alternating and random copolymers, composition of interpolymer complex formed between PS-PEO block copolymers and PAA is constant (e.g 1:1 unit mole ratio of reacting units) and independant on solvent composition and molecular characteristics of the copolymer. The conformation of the block copolymer in the presence of mixed solvents or even micellization does not in any way affect its ability to form complexes with PAA. Reduced viscosity behaviour during complex formation may well reveal these facts.

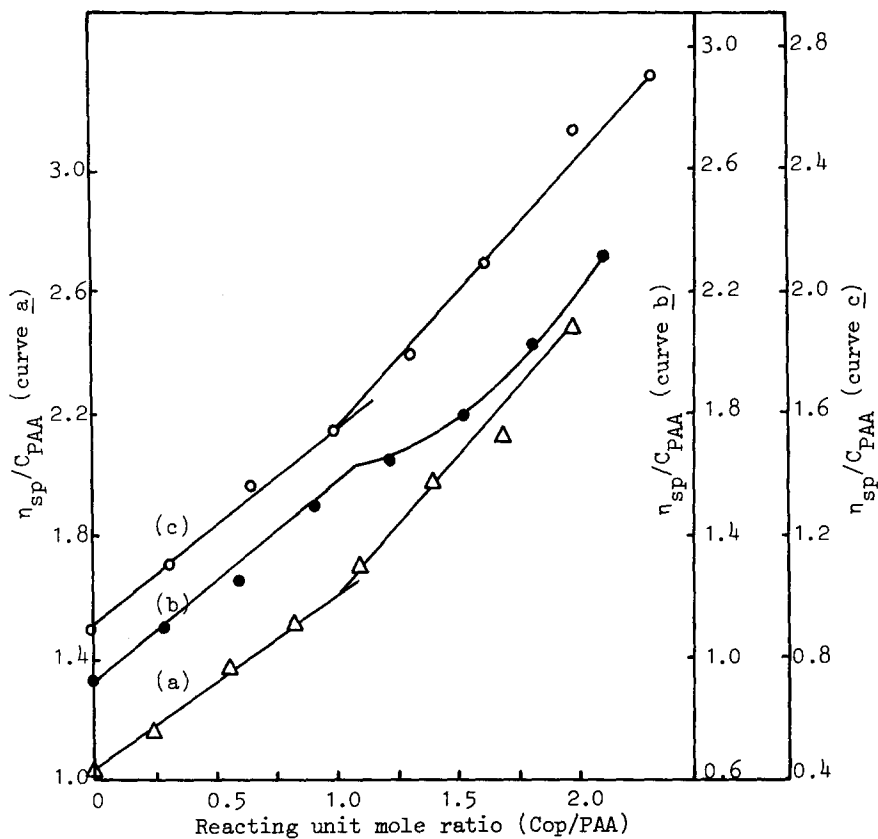


Fig. 5 : Reduced viscosity ( $\eta_{sp}/C_{PAA}$ ) change during complex formation between different block copolymers PS-PEO and PAA in 30 % water + 70 % THF

- a) diblock copolymer (sample 32)
- b) diblock copolymer (sample 36)
- c) triblock copolymer (sample 24)

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