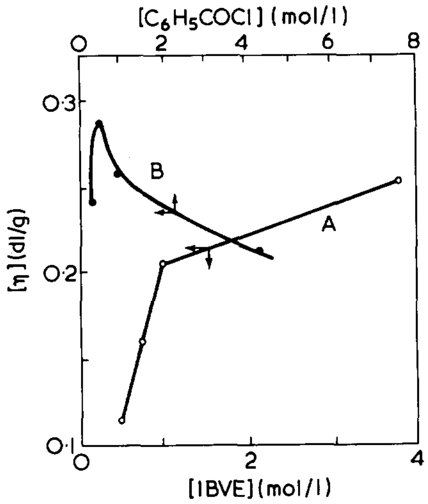

Figure 2 A, Variation of [η] with [IBVE]; [C_6H_5COCl] = 0.75 mol/l; B, Dependence of [η] on [C_6H_5COCl]; [IBVE] = 1.25 mol/l

latter instance, the slope change also occurs at 1 M vinyl ether concentration. Such a feature implies that above this threshold [IBVE] monomer transfer assumes dominance over other chain breaking reactions.

Monomer specificity

n-Butyl vinyl ether and *N*-vinyl carbazole have also been observed to undergo facile polymerization in presence of C_6H_5COCl at ambient temperatures. For the polymerization of *N*-vinyl carbazole by C_6H_5COCl, as in the case with $POCl_3$, $SOCl_2$ and CrO_2Cl_2 no colouration was developed in the polymerization system or in the product polymer indicating the absence of charge transfer interactions[15].

CONCLUSION

Benzoyl chloride can initiate the polymerization of vinyl ethers and *N*-vinyl carbazole by a conventional cationic mechanism. As a cationic initiator for IBVE polymerization, benzoyl chloride behaves differently from chromyl chloride in several respects.

ACKNOWLEDGEMENTS

The authors thank the authorities of the Indian Institute of Technology, Kharagpur, for facilities.

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Titrimetric studies of *p*-aminobenzoic acid–formaldehyde–*p*-bromophenol copolymers in non-aqueous media

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(Received 11 August 1977; revised 16 November 1977)

The need to measure functional groups in polymers on a quantitative basis has assumed importance in recent years. Preliminary studies on some synthetic copolymers having acidic and basic functional groups, revealed that the structure, composition and the total acidity/basicity in a given weight of the copolymer, could be correlated with their titration curves in non-aqueous media[1,2]. Therefore, it was considered of interest to see whether such an approach could be extended to a copolymer having different types of acidic and basic functional groups present together. Keeping this fact in view, a copolymer obtained by the condensation of *p*-aminobenzoic acid, formaldehyde, and *p*-bromophenol has been chosen for this investigation. This system is interesting in view of the fact that from the Br content of the copolymer one can calculate the total amount of each of the functional groups, e.g. OH, COOH, and NH_2 groups present in a given weight of the copolymer. The titration curves in non-aqueous media of the copolymer and the various fractions separated from it, indicated an excellent correlation between calculated and observed amounts of the various functional groups. Apart from this, some of the functional groups were found to be hyperacidic or hyperbasic in the copolymer chain. The enhanced acidic or basic character of the functional groups could be attributed to intramolecular hydrogen bonding between neighbouring groups in the copolymer chain. An attempt has been made to correlate these observations with composition and structure of the copolymers.

EXPERIMENTAL

p-Aminobenzoic acid–formaldehyde–*p*-bromophenol copolymer (I) was prepared by refluxing a mixture of *p*-aminobenzoic acid (0.5 mol), *p*-bromophenol (0.5 mol) and formaldehyde (1.0 mol), in the presence of 2 ml of 10N HCl for 3 h at 130°C. The reaction mixture was then poured in ice water and the precipitated product washed several times with distilled water to remove unreacted monomers. The polymer yield was about 80%. The copolymer thus obtained was then fractionated by dissolving about 10.0 g of the product in pyridine, the higher

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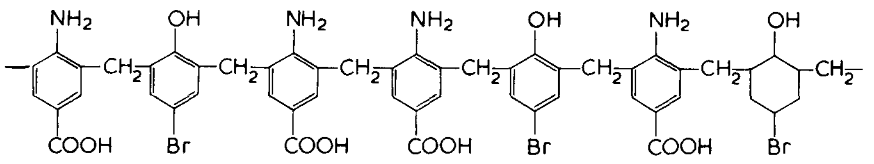

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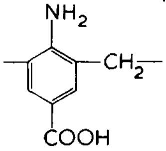

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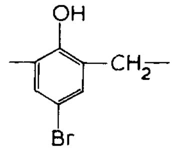

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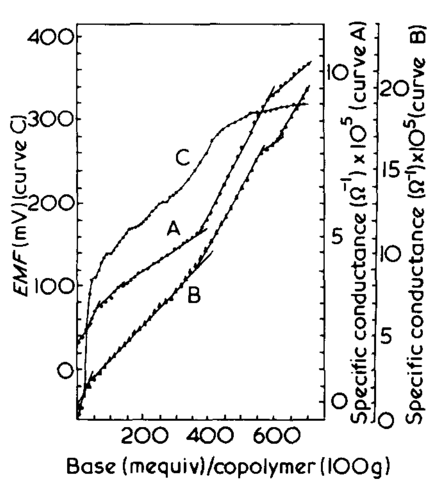

Figure 1 Titration curves of copolymer (I) in pyridine. A, Conductometric curve with sodium methoxide; B, Conductometric curve with TMAH; C, Potentiometric curve with sodium methoxide

molecular weight fractions being separated by the addition of water as nonsolvent. Approximately 0.5, 0.7, 2.6, 3.3 and 2.9 g of the copolymers separated at five consecutive stages of separation. The Br content of the conglomerate and the fractions were determined by Volhard's method[4].

A Radiometer pH meter (model pHM 26c) with a glass (G202E) and a calomel (K401) electrode as reference was used for potentiometric titrations, and a Leeds and Northrup conductance bridge (4959) was used for conductometric titrations. The details of the titration procedure have been reported elsewhere[3].

RESULTS AND DISCUSSION

Figure 1 shows the conductometric and potentiometric titration curves of the copolymer (I) in pyridine with sodium methoxide and tetramethyl ammonium hydroxide (TMAH) as titrant bases. The copolymer chains contain two types of distinct repeating units (II and III), which are either linked in a completely random manner, or there may be a small block of one type of repeating unit followed by another block of the other repeating unit. On the basis of Br estimation of the copolymer and the fractions, one can calculate the probable proportion of the respective repeating units present in the copolymer chain. From the composition of the copolymers thus obtained, the total amount of each of the functional groups, e.g. OH, COOH, and NH_2 groups in a given weight of the copolymer could be evaluated. The conductometric titration curves with sodium methoxide of the copolymer (e.g. curve A of *Figure 1*), and the 5 fractions showed a final break, which represents the neutralization of total acidic groups (e.g. COOH and OH) in a given weight of the copolymer. The observed values tallied within experimental error with the calculated values of OH and COOH groups. However, the copolymer and the 5 fractions when titrated in the same medium with TMAH as titrant base, invariably did not indicate the complete neutralization of the acidic functional groups. The potentiometric titration curves of the conglomerate and the various fractions in pyridine with sodium methoxide as titrant base showed a series of inflections. In the case of latter fractions, e.g. 3, 4 and 5, the final inflection is quite sharp, and it represents the neutralization of total acidic groups (e.g. OH and COOH). However, complete neutralization was not observed in the potentiometric curve for the conglomerate and the first two fractions. Since the latter fractions have a comparatively larger proportion of *p*-bromophenol repeating unit, it therefore seems likely that some of these features of the titration curves are related to the composition of the copolymers.

For the estimation of NH_2 groups, potentiometric and conductometric titrations of the copolymer and the 5 fractions have been carried out in glacial HAc with perchloric acid as titrant acid. The conductometric titration curves of the conglomerate (e.g. curve A of *Figure 2*) and the various fractions showed a final break which coincided (within experimental error) with the calculated amount of NH_2 groups. *Table 1* gives the mole fraction of the constituents, % age of Br, smallest interval and the calculated and observed

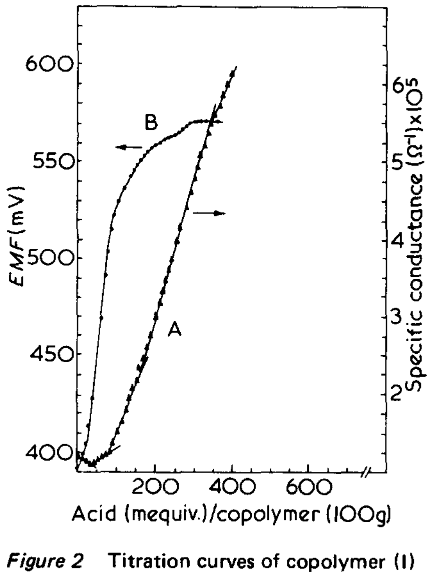

Figure 2 Titration curves of copolymer (I) in glacial HAc with perchloric acid. A, Conductometric curve; B, potentiometric curve

Table 1 Calculated and observed amounts of functional groups in *p*-aminobenzoic acid–formaldehyde-*p*-bromophenol copolymer (I). Values expressed in milliequivalents of acid/base per 100 g of copolymer

Copolymer	Br (% age)	Mole ratio PBP : PAB	NH_2 groups Calculated	NH_2 groups Observed	Total acidic groups (COOH + OH) Calculated	Total acidic groups (COOH + OH) Observed
Conglomerate	23	0.94:1.06	319	340	603	590
Fraction 1	10.1	0.41:1.59	508	485	639	645
Fraction 2	11.6	0.47:1.53	488	490	635	645
Fraction 3	15.0	0.61:1.39	440	445	632	640
Fraction 4	17.4	0.70:1.30	220	225	620	615
Fraction 5	41.18	1.67:0.33	92	95	558	550

* Calculated values are on the basis of Br estimation

amounts of OH, COOH, and NH_2 groups per 100 g of copolymer. The final inflection of the potentiometric curves of the fractions 3, 4 and 5 only, coincided with the complete neutralization of NH_2 groups. As stated earlier, this may be related to the composition of the copolymers.

The most interesting feature of the titration curves is the presence of a 'smallest interval' between any two consecutive breaks/inflections, and the remaining breaks or inflections in the titration curves occur in simple multiples of this smallest interval. The smallest interval has been found to be different for the copolymer and the various fractions. Of course, this interval is identical for a particular fraction, irrespective of whether it is titrated with an acid or a base. The fact that some of the functional groups in the copolymer chain have been neutralized in a stepwise manner, indicates that they have hyperacid/hyperbasic character. This enhanced acidity/basicity could be attributed to intramolecular hydrogen bonding between neighbouring functional groups. Indeed, infra-red spectra of the copolymer and all the fractions indicated sharp absorptions in the range 3450–3600, and 3070–3350 cm^{-1}, showing the probable presence of $O{-}H\cdots O$ and $N{-}H\cdots N$ intramolecular hydrogen bonding. Of course, the presence of such hydrogen bonding has already been reported in phenolic oligomers from infra-red[5], conformational[6] and titrimetric studies[7]. The more distinct stepwise neutralization of the functional groups in conductometric titration curves compared to potentiometric curves may be due to the formation and different degree of dissociation of acid–anion or base–cation complexes which might be present in a medium of low dielectric constant. As expected, these effects had little influence on the potentiometric curves. Moreover, the formation of homoconjugate complexes in a medium of low dielectric constant may also have pronounced influence on the nature of the conductometric titration curves[8].

Thus non-aqueous titrations may provide a rapid and convenient method for determining the relative amounts of different repeating units present in copolymers with acidic and basic functional groups.

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Molecular interpretation of correlation between polymer glass transition T_g and an e.s.r. parameter T_{50G}

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(Received 1 September 1977; revised 22 November 1977)

INTRODUCTION

It has been shown that the glass transition temperature, T_g, of polymers can be measured by means of nitroxide spin probes incorporated in the polymer matrix[1–4]. In particular, the so-called T_g, T_{50G} correlation, first reported by Rabold[1] and semiquantitatively characterized by Kumler and Boyer[4] using 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (BzONO) radicals, is a valuable tool for T_g determination because T_{50G} can be measured straightforwardly. T_{50G} is the temperature at which the separation of the outermost peaks of the electron spin resonance (e.s.r.) spectrum of probes in polymer matrix is 50 G (gauss). The bulky nitroxide radicals which experience the dynamic state of their microenvironment are supposed to be located in amorphous regions of polymers. Thus it seems probable that the T_g, T_{50G} correlation will be a potential method for determining T_g for non-homogeneous polymer systems, e.g. polymer blends, filled and reinforced polymers. Therefore, the molecular origin of the T_g, T_{50G} correlation should be exactly determined. Here we have studied this relationship for some amorphous carbon backbone polymers which can be regarded as one phase systems. The experimental results are explained quantitatively on the basis of thermally activated motions of polymer segments.

EXPERIMENTAL

Materials

E.s.r. measurements were carried out with the following high molecular weight polymers: polyisobutylene (PIB) Oppanol B 200 obtained from BASF; poly(ethyl acrylate) (PEA) and poly(methyl acrylate) (PMA) from Röhm; poly(vinyl acetate) (PVAc) from Hoechst and suspension polymerized poly(vinyl chloride) (PVC) from BASF.

Methods

The spin probe radical BzONO was prepared according to the method of Rozantsev[5]. Solid BzONO at a concentration of 100 ppm was added to a solution of polymer in an appropriate solvent. A solid sample was obtained by evaporation of the solvent. The resultant sample was dried in a vacuum oven at 313–323K overnight. E.s.r. spectra were recorded over a suitable temperature range using an AEG 12 X spectrometer equipped with a temperature accessory. The measurement conditions were controlled to avoid overmodulation and saturation effects[6]. The parameter T_{50G}, related to the tumbling frequency of the paramagnetic probe with an effective frequency of

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0032–3861/78/1905–0598 $01.00