Benzoyl chloride as an initiator of cationic polymerization

Mukul Biswas and G. M. Absanul Kabir
Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

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INTRODUCTION

There appears to be no report to the effect that benzoyl chloride can act as an initiator for the cationic polymerization of vinyl monomers. In continuation of our work[1–5] on the elucidation of the initiation characteristics of some oxychlorides of group V and VI elements, we have observed that benzoyl chloride can induce the conventional cationic polymerization of isobutyl vinyl ether (IBVE) with some distinctive features which are described in this paper.

EXPERIMENTAL

Materials

IBVE (Merck, Germany) was purified and distilled following recommended procedures. Solvents, all of analytical grade, were purified and fractionated by standard methods.

Benzoyl chloride (BDH) was distilled *in vacuo*, collected in a stoppered pyrex vessel and stored in a dry glove box in the dark.

Polymerization

All preparations and dilutions of solutions were carried out in a dry glove box[6]. The polymerizations were conducted in pyrex reaction vessels[3,4,6] under nitrogen. The polymers were precipitated by addition of methanol, collected and conditioned following the procedure of Eley and Richards[7].

The intrinsic viscosities of the polymer samples were determined in benzene at 32°C.

RESULTS AND DISCUSSION

Kinetic characteristics

At concentrations of C_6H_5COCl from ~0.2–1.0 M the polymerizations proceed without any induction period to high conversions, the time–conversion curves (*Figure 1a*) tending to become explosive at higher concentrations of C_6H_5COCl. However, for $[C_6H_5COCl] \approx 10^{-2}$ M, no polymerization could be detected with 1.25 M [IBVE] even after 1 h. The polymerization order in carbon tetrachloride, with respect to C_6H_5COCl concentration varying from 0.2–1.0 mol/l, is 2 (*Figure 1b*, curve A). At a constant concentration of C_6H_5COCl the polymerization is first order (*Figure 1b*, curve B) in [IBVE], the latter ranging from 0.5 to 1.25 mol/l. In the case of polymerization of IBVE by chromyl chloride[8] the corresponding orders are 1 and 2, respectively. The polymerization is totally inhibited by pyridine which indicates the cationic nature of the reaction.

The second order dependence of the rate on C_6H_5COCl concentration appears to be consistent with an initiation scheme involving self-ionization of two molecules of C_6H_5COCl as in:

$$2C_6H_5COCl \rightleftharpoons C_6H_5CO^+ + C_6H_5COCl_2^-$$

The polymerization may then be initiated through a direct interaction between IBVE and $C_6H_5CO^+$ cations. It may be significant to recall in this context our earlier observations that for α-methylstyrene–$POCl_3$[1], *N*-vinyl carbazole–$SOCl_2$[4]/$VOCl_3$[5] and IBVE–CrO_2Cl_2[8] polymerization systems, the kinetics are consistent with a first order ionization of the appropriate oxychloride.

Molecular weight trends

Figure 2 represents the variation of intrinsic viscosity of the polymers with the concentrations of C_6H_5COCl and IBVE, respectively. The maximum observed in the $[\eta]-[C_6H_5COCl]$ plot is of rare occurrence and is reminiscent of the situations encountered by Zlamal[9] for isobutene–$AlCl_3$, Vesely[10] for isobutene–$TiCl_4$ and by Biswas and John[11] for *N*-vinyl carbazole–RMgX polymerization systems. Interestingly, for vinyl ether–chromyl chloride systems[8,12] the $[\eta]$ values have been observed to be independent of the chromyl chloride concentration. However, in the light of above observations and the generalizations made by Plesch[13], the initial rise in $[\eta]$ with C_6H_5COCl concentration may correspond to the removal, by the initiator, of some basic impurities participating in the chain breaking reaction. The exact nature of this impurity is obscure, although adventitious water may be one possibility. The subsequent fall in $[\eta]$ with further increase in C_6H_5COCl concentration may imply participation of initiator fragments $[C_6H_5COCl_2^-]$ in chain breaking, since according to the ionization scheme given above $[C_6H_5COCl_2^-]$ would be equal to $K^{1/2}$ $[C_6H_5COCl]$, K being the equilibrium constant for the proposed ionization.

The $[\eta]$ *versus* [IBVE] plot indicates a slope change at a particular IBVE concentration of ~1 M. Similar behaviour has been observed for the alkyl vinyl ether–$BF_3.Et_2O$[14], $SnCl_4$[7] polymerization systems by Eley *et al.* and also for the n-BVE[12] and IBVE[8]–chromyl chloride system by the authors. In the

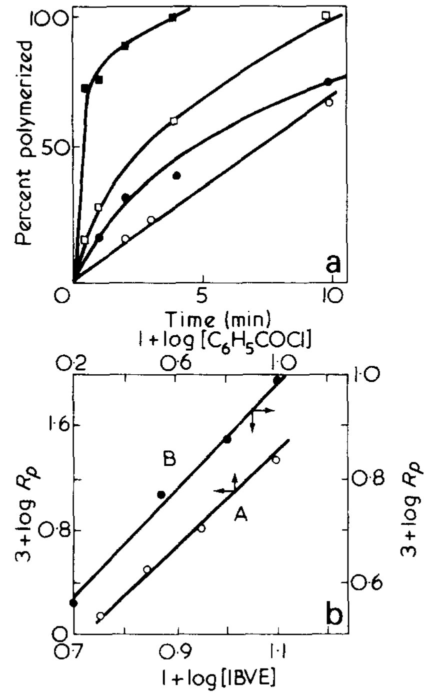

Figure 1 (a) Time–conversion curves for benzoyl chloride initiated polymerization of IBVE in CCl_4 at 32°C. [IBVE] = 1.25 mol/l; $[C_6H_5COCl]$ = ○, 0.2 mol/l; ●, 0.3 mol/l; □, 0.5 mol/l; ■, 1.0 mol/l.
(b) A, Dependence of log R_p on log $[C_6H_5COCl]$. [IBVE] = 1.25 mol/l; solvent, CCl_4; temperature, 32°C. B, Dependence of log R_p on log [IBVE]; $[C_6H_5COCl]$ = 0.75 mol/l; solvent, CCl_4; temperature, 32°C

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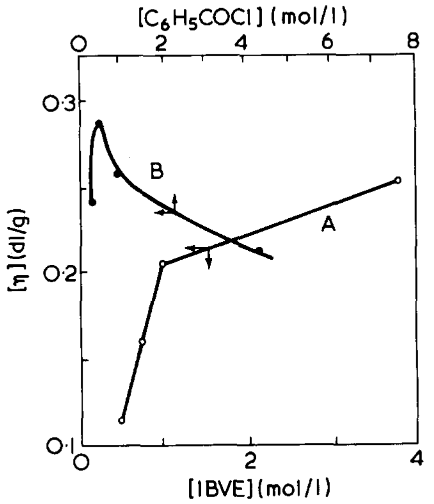

Figure 2 A, Variation of [η] with [IBVE]; [C_6H_5COCl] = 0.75 mol/l; B, Dependence of [η] on [C_6H_5COCl]; [IBVE] = 1.25 mol/l

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.

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REFERENCES

1 Biswas, M. and Mishra, P. K. *Polymer* 1975, **16**, 621
2 Biswas, M. and Kabir, G. M. A. *Polymer* 1978, **19**, 357
3 Biswas, M. and Mishra, P. K. *J. Polym. Sci. (Polym. Lett. Edn)* 1973, **11**, 639
4 Biswas, M. and Kamannarayana, P. *J. Polym. Sci. (Polym. Chem. Edn)* 1975, **13**, 2035
5 Biswas, M. and Kamannarayana, P. *J. Polym. Sci. (Polym. Chem. Edn)* 1975, **14**, 2071
6 Biswas, M. and Chakravorty, D. *J. Polym. Sci. (Polym. Chem. Edn)* 1973, **11**, 7
7 Eley, D. D. and Richards, A. W. *Trans. Faraday Soc.* 1949, **45**, 425
8 Biswas, M. and Kabir, G. M. A. *Eur. Polym. J.* 1978 in press
9 Zlamal, Z. *J. Polym. Sci.* 1957, **24**, 285
10 Vesely, K. *J. Polym. Sci.* 1958, **30**, 375
11 Biswas, M. and John, K. J. *J. Polym. Sci. (Polym. Chem. Edn)* 1978 in press
12 Biswas, M. and Kabir, G. M. A. *J. Polym. Sci. (Polym. Chem. Edn)* 1978, in press
13 Plesch, P. H. 'The Chemistry of Cationic Polymerization', Pergamon Press, New York, 1963, p.198
14 Coombes, J. D. and Eley, D. D. *J. Chem. Soc.* 1975, p.3700
15 Ellinger, L. P. 'Advances in Macromolecular Chemistry', (Ed. W. M. Pasika) Academic Press, 1968, Vol 1, p.169

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

S. K. Chatterjee and L. S. Pachauri
Department of Chemistry, Delhi University, Delhi-7, India
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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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