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Preliminary Study of Cationic Copolymerization of α-Methyl-Styrene and Isobutyl Vinyl Ether I

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Introduction

While styrene and isobutyl vinyl ether (IBVE) can be copolymerized using γ-ray for initiation (free ion mechanism) as shown by UENO, et al. (1966) and HAYASHI, et al. (1973); they can not be copolymerized using chemical initiators (ion-pair mechanism) due to very high reactivity of IBVE, according to the latter authors. Extensive study of copolymerization of 2-chloroethyl vinyl ether with styrene and its derivatives was carried out by MASUDA and HIGASHIMURA (1971). They reported that the styrene incorporation in the copolymer increased using a more polar solvent and/or a stronger Lewis acid, i.e. increasing the charge separation. These results suggested that using a weakly nucleophilic counteranion can probably induce satisfactory copolymerization between styrene or α-Methyl-Styrene (α-MS) and a vinyl ether.

We have studied cationic copolymerization of α-MS and IBVE using "H_2O"/$EtAlCl_2$ initiator system and CH_2Cl_2 solvent. A preliminary report of the results obtained is presented here.

Experimental

α-MS, IBVE and CH_2Cl_2 were freshly distilled over CaH_2 and also stored over it at low temperatures. $EtAlCl_2$ (Ethyl Corp.) was used as received.

All experiments were carried out in a stainless steel dry box under nitrogen (30 ppm moisture). To a precooled mixture of monomers and solvent in a three necked flask, $EtAlCl_2$ solution (1.5 M in hexane) was dropwise added with rapid stirring. The reaction was

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stopped after 15 minutes by adding 5 ml MeOH. The copolymer was precipitated in excess MeOH, filtered and dried.

Copolymer composition was determined using NMR spectra recorded using $CDCl_3$ solvent on JOEL FX 60 Q model. The Differential Thermal Analysis (DTA) was carried out using Du Pont model 900. The heating rate was 20°C/min. under nitrogen.

Result and Discussion

The synthesis of homo- as well as copolymerizations of α-MS and IBVE were carried out using "H_2O"/$EtAlCl_2$ initiator system and CH_2Cl_2 solvent at -50°C. "H_2O" refers to the advantitious impurity, most probably water, acting as a source of initiating protons (KENNEDY, TRIVEDI 1978). The effect of monomer feed composition on the copolymer yield and composition is shown in Table 1.

TABLE 1

Effect of monomer feed composition on the copolymer yield and composition at -50°C.

α-MS in feed							
mole %	100	93	90	75	50	10	0
yield gms	61	5	23	13	11	7	11
α-MS in copolymer							
mole %	100	68	79	30	9	1	0

CH_2Cl_2 100 ml, α-MS+IBVE = 100 ml, $EtAlCl_2$ = $1\text{-}5\times10^{-3}$ M.

A runaway reaction was obtained for the homopolymerization of α-MS, giving very high yield. However, addition of even small amounts of IBVE in the feed significantly reduced the yield. Yields were low even for the homopolymerization of IBVE, signifging presence of an efficient chain terminating reaction. This is in contrast to BAWN, et al. (1971) and CHUNG, et al.(1975), who found efficient chain transfer and near absence of termination for the IBVE polymerization using $SbCl_6^{\ominus}/CH_2Cl_2$ system. They reported low molecular weights (~10000) as against high molecular weights (~200000) of PIBVE for our system (TRIVEDI, 1979).

These results suggest that possibly chain transfer reaction is absent in our system. While a detailed discussion regarding the molecular weights with reference to the reaction mechanism will be published elsewhere (TRIVEDI, 1979), a confirmation indicating the presence of random copolymers is provided.

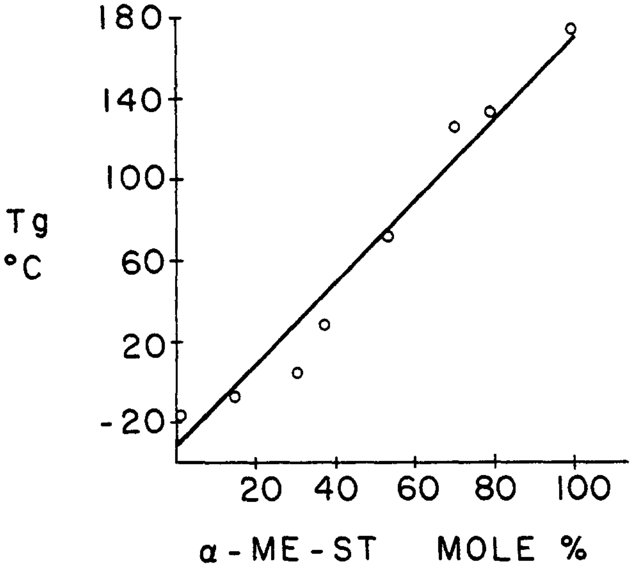

Fig. 1. Effect of copolymer composition on its glass transition temperature.

The glass transition temperature, Tg, of the copolymer as a function of copolymer composition is shown in Figure 1. There is a steep increase in Tg as α-MS content increases in the copolymer, clearly proving that it is a random copolymer. The small deviations can be explained as due to low molecular weight of copolymer relative to homopolymers (TRIVEDI 1979) and non-uniformity of the composition. In fact for some samples along with one major Tg peak, some minor peaks can be observed, indicating heterogeneous nature of copolymer chains. The data shown here refers to major Tg peaks only.

Conclusion

Random copolymerization between α-MS and IBVE was successfully carried out using "H_2O"/$EtAlCl_2$/CH_2Cl_2 system at -50°C. Due to large reactivity of IBVE, its incorporation in the polymer chain is substantial even at low feed concentration. DTA data confirms the presence of random copolymer. An efficient chain termination giving low yields in homo- and copolymerization of IBVE was detected.

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Summary

Cationic copolymerization of α-MS and IBVE was successfully carried out using "H_2O"/$EtAlCl_2$ initiator system and CH_2Cl_2 solvent at -50°C. The effect of monomer feed concentration on the copolymer yield and composition was studied. Small concentrations of IBVE had significant effect on the copolymer yield and composition, while that of α-MS had only marginal effect. Tg of the copolymers was linearly dependent on the α-MS content strongly indicating that the copolymerization was of random nature.

Reference:

1. BAWN, C.E.H., FITZSIMMONS, C., LEDWITH. A., PENFORD, J., SHERRINGTON, D.C. and WEIGHTMAN, J.A.; Polymer 12, 119 (1971)
2. CHUNG, Y.J., ROONEY, J.M., SQUIRE, D.R. and STANNETT, V.: Polymer 16, 527 (1975)
3. HAYASHI, K., HAYASHI, K. and OKAMURA, S.: Polymer J. 4, (5) 495 (1973)
4. KENNEDY, J.P. and TRIVEDI, P.D.: Adv. in Polymer Sci. 28, 91 (1978)
5. MASUDA, T. and HIGASHIMURA, T.: J. Macromol. Sci.-Chem. A5, 549 (1971)
6. TRIVEDI, P.D.: Submitted to J. Macromol. Sci.-Chem. (1979)
7. UENO, K., HAYASHI, K. and OKAMURA S.: Polymer 7, 431 (1966)

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