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The reactivities of polymer radicals towards stilbene; the cases of vinyl methyl ketone, isopropenyl methyl ketone, styrene and α-methylstyrene

C.A. Barson[1], K. Behari* and J.C. Bevington[2]**

[1]Department of Chemistry, University of Birmingham, Birmingham B15 2TT, UK
[2]Department of Chemistry, University of Lancaster, Lancaster LA1 4YA, UK

Summary

^{14}C-stilbene has been used for measurement of the incorporation of stilbene in polymers of vinyl methyl ketone, isopropenyl methyl ketone and styrene, and in copolymers of the two ketonic monomers and of styrene with α-methylstyrene. It has been confirmed that the introduction of an α-methyl group into a monomer significantly reduces the reactivity of the derived polymer radical towards stilbene.

Introduction

Stilbene (STL) is considerably more reactive towards polymer radicals derived from certain monomers represented as CH_2:CHX than towards the radicals corresponding to the related monomers CH_2:C(CH_3)X having a methyl group at the alpha position. The effect has been demonstrated for X = CN (1,2) and X= $COOCH_3$ (3) by determining monomer reactivity ratios for the copolymerizations of the various monomers with STL and then calculating the velocity constants for the cross-propagations involving STL as monomer. Separate studies of end-groups in polymers prepared in the presence of STL have revealed that it is very reactive towards the benzoyloxy radical but not towards the 2-cyano-2-propyl radical (4). These characteristics can be correlated on the basis that steric effects are of great importance in the reactions of radicals with STL, the restrictions being least for the oxygen-centred benzoyloxy radical and greatest for those radicals in which the unpaired electron can be represented as being at a carbon atom also having two sizable groups attached to it.

The study of reactivity of STL towards polymer radicals has now been extended to the cases where X= $COCH_3$ (monomers, vinyl methyl ketone (VMK) and isopropenyl methyl ketone (IPMK)) and X = C_6H_5 (monomers, styrene (STY) and α-methylstyrene (MST)). As previously, copolymerizations were performed with ^{14}C-STL so that it was possible to make accurate measurements of its incorporation in polymers even at very low levels. The ceiling temper-

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* On study leave from the University of Allahabad, India
** To whom offprint requests should be sent

ature for the polymerization of MSTY is quite low (5) and ordinarily its radical homopolymerization is slow at temperatures in the region of 40 to 50°C; it was therefore not practicable to study directly its copolymerization with STL. Radical copolymerizations of STY with MSTY at 60°C proceed quite readily (6) and so the reactivity of STL towards a polymer radical with a MSTY unit at its reactive end was examined by considering ternary copolymerizations of STY, MSTY and STL.

Experimental

Procedures for preparation of polymers and their subsequent assay for carbon-14 content were essentially as reported previously (2,3). Monomers were purified by fractional distillation in N_2 at reduced pressure.

Polymerizations involving the ketonic monomers were performed under air-free conditions at 60°C using a mixture of dimethylformamide and toluene (4:3 by volume) as diluent. Azobis(isobutyronitrile) at 6.0×10^{-3} mol dm^{-3} was used as initiator and, in each case, the total concentration of monomers was close to 3.30 mol dm^{-3}. The concentration of ^{14}C-STL in the systems was fixed at 2.24×10^{-2} mol dm^{-3}; its specific activity was 5.07×10^4 Bq g^{-1}. The times required for approx. 15% conversion ranged from 2 hours for the system containing VMK and STL to 20 hours for that containing IPMK and STL. The polymerizations involving STY and MSTY were performed with toluene as diluent, with monomers at a total concentration of close to 3 mol dm^{-3} and with azobis(isobutyronitrile) and ^{14}C-STL (specific activity, 1.44×10^4 Bq g^{-1}) at concentrations of 1.0×10^{-2} and 3.05×10^{-2} mol dm^{-3} respec.; conversions were restricted to 10%. Polymers were recovered by precipitation in methanol, purified by two reprecipitations and dried in vacuum; tests involving appropriate unlabelled polymers mixed in solution with ^{14}C-STL showed that the procedure was satisfactory for elimination of occluded radioactive material.

Results and Discussion

The specific activity of the polymer prepared from VMK and ^{14}C-STL in the molar ratio 165.3 : 1 was 57.5 Bq g^{-1}. Comparison of the specific activities of the polymer and the original ^{14}C-STL shows that the polymer can be represented as $(C_4H_6O)_{2266}(C_{14}H_{12})_1$. As shown in Figure 1, the specific activities of the polymers fell as VMK in the feed was replaced by IPMK. The polymer formed from IPMK and ^{14}C-STL (molar ratio 136:1) had a specific activity of 3.5 Bq g^{-1} and therefore its composition can be expressed as

$(C_5H_8O)_{31020}(C_{14}H_{12})_1$. When one of the monomer reactivity ratios (r_b) is very small and also $(M_a/M_b)_{feed}$ is large, the copolymer composition equation can be simplified to

$$\left[\frac{M_a}{M_b}\right]_{copolymer} = \left[\frac{M_a}{M_b}\right]_{feed} \times r_a$$

Taking M_a and M_b as the ketonic monomer and STL respectively, values of r_a of 13.7 (VMK) and 228 (IPMK) are found. The corresponding quantities for methyl acrylate and methyl methacrylate with STL (3) are 3.9 and 423, leading to approximate values for the velocity constants for the reactions of STL with the poly(methyl acrylate) and poly(methyl methacrylate) radicals at 60°C of 510 and 1.6 $dm^3\ mol^{-1}\ s^{-1}$ respectively.

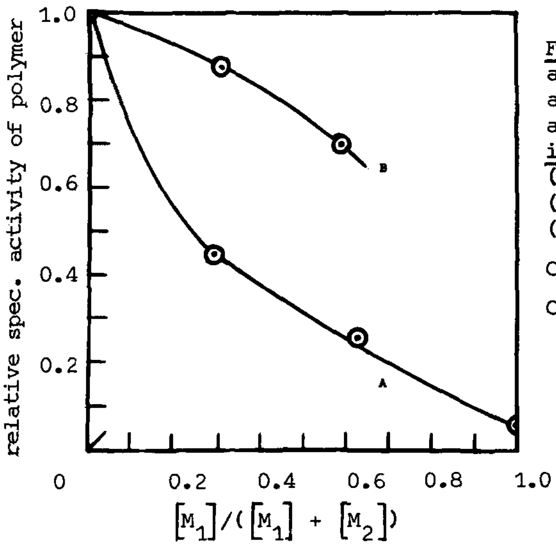

Figure 1. Relative specific activities of polymers prepared with labelled stilbene and various mixtures of (i) isopropenyl methyl ketone (IPMK) and vinyl methyl ketone (VMK) and (ii) α-methylstyrene (MSTY) and styrene (STY).

Curve A: M_1 = IPMK, M_2 = MVK

Curve B: M_1 = MSTY, M_2 = STY

The values found for r_a do not by themselves allow a direct comparison of the reactivities of STL towards the polyVMK and polyIPMK radicals; for that comparison to be made, it is necessary to have information on the values of k_p for the homopolymerizations of the ketonic monomers and these values are not available. It is probable however that k_p for VMK is the larger so that at 60°C the velocity constant for the reaction of the polyVMK radical with STL exceeds that for the corresponding reaction of the polyIPMK radical by a factor exceeding the ratio of the two values of r_a, i.e. greater than 16.6.

Figure 1 also shows result for the system STY/MSTY/^{14}C-STL. It is evident that the introduction of the α-methyl substituted monomer into the feed affected the specific activity of the resulting polymer to a much smaller extent than for the ketonic monomers. The specific activity of the polymer derived from the system containing STY but without MSTY was 16.4 Bq g^{-1}, indicating that the polymer could be represented as containing 1525 STY units for each STL unit. The value of (STY/STL) in the feed was 116 so that r_a is found to be 13; a value of 11 was found previously (7).

It is necessary to consider the possibility that the decrease in the specific activities of the polymers with increasing content of MSTY in the feed might be due simply to the replacement of some C_8H_8 units by the heavier C_9H_{10} units. The compositions of the polymers prepared from mixtures of STY, MSTY and STL have been calculated on the assumption that the presence of a low concentration of STL in the reacting system has no effect on the relative numbers of the units derived from the two principal monomers. Taking STY as monomer-1 for the copolymerization with MSTY, r_1 at 60° has been taken as 1.5 (6) and r_2 as 0.6 (8). For the two ternary copolymerizations, (STY/MSTY) in the feed had values of 2.29 and 0.72, leading to values of (STY/MSTY) in the copolymers of 3.48 and 1.13. The formula weights of the average monomeric units in the two copolymers are therefore

$$\frac{(3.48 \times 104) + (1 \times 118)}{4.48} \quad \text{and} \quad \frac{(1.13 \times 104) + (1 \times 118)}{2.13}$$

i.e. 107 and 110 respectively. The specific activities of the two copolymers were found to be 14.4 and 11.4 Bq g^{-1}. If the presence of MSTY in the ternary systems had no effect on the incorporation of STL, the predicted specific activities of the two ternary copolymers are (16.4 x 104)/107 and (16.4 x 104)/110 i.e. 15.9 and 15.5 Bq g^{-1}, values which are appreciably greater than those observed. It appears therefore that the introduction of MSTY into the reaction mixture depresses the rate of incorporation of STL, suggesting that the polyMSTY radical is comparatively unreactive towards STL. As explained in the Introduction, it was not practicable to examine directly the binary copolymerization of MSTY with STL but the trend in the results clearly suggests that r_a would be appreciably smaller than for the system of STY with STL. Rudin and Chiang (8) used values of 176 and 26 $dm^3\ mol^{-1}\ s^{-1}$ for k_p at 60°C for STY and MSTY respectively; the factor of nearly seven between the two quantities causes a further increase in the expected direction of the difference between the velocity constants for the reactions of polySTY and polyMSTY radicals with STL. It must be concluded that the systems considered here also show the effect of an alpha methyl group in reducing quite markedly the reactivities of polymer radicals towards STL.

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