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The reactions with initiating radicals of monomers having low ceiling temperatures

The cases of 2-isoprophenylnaphthalene with the 1-cyano-1-methylethyl and the benzoyloxy radicals

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Summary

End-group analyses of copolymers of 2-isopropenylnaphthalene (iPN) with methyl methacrylate have been used to compare the reactivities of the monomers towards the 1-cyano-1-methylethyl and benzoyloxy radicals. It is found that iPN is very similar to 2-vinylnaphthalene in its reactivity towards these initiating radicals. In this respect, the results resemble those for the pair styrene and alpha-methylstyrene. The monomers containing the naphthyl group are appreciably more reactive than those containing the phenyl group.

Introduction

Reports have already been given on the reactions of the benzoyloxy and 1-cyano-1-methylethyl radicals with monomers, such as alpha-methylstyrene (1,2) and alpha-methoxystyrene (3), having low ceiling temperatures; the work has now been extended to 2-isopropenylnaphthalene (iPN). This monomer gives rise to polymers and various types of copolymer which have attracted interest (4). Anionic polymerization at moderately low temperatures gives a homopolymer with a glass-transition temperature as high as 220°C. A rather slow radical copolymerization at 80°C with n.butyl methacrylate has been described (5). Monomer reactivity ratios for a few radical copolymerizations involving iPN have been quoted (6). Use has been made of iPN in preparations of samples of poly(methyl methacrylate) (polyMMA) containing a few pendant naphthyl groups, to be used in spectroscopic studies (7).

Well documented procedures were used in the work now described. The reactivity of iPN towards the 1-cyano-1-methylethyl radical was studied by examination by means of ^{13}C-NMR of the end-groups in a copolymer with MMA, prepared using azobis(isobutyronitrile) ^{13}C-enriched in its methyl groups (^{13}C-AIBN) as initiator (1). The study of the reaction of iPN with the benzoyloxy radical depended upon comparisons of the numbers of benzoate and phenyl end-groups in a copolymer with MMA, prepared using benzoyl peroxide labelled with carbon-14 in the carbonyl groups and with tritium in the rings

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(^{14}C,^{3}H-BPO) (2). An attempt was also made to apply the procedure used with the 1-cyano-1-methylethyl radical for the study of the benzoyloxy radical. Peroxide, ^{13}C-enriched at the carbonyl sites (^{13}C-BPO), was used to initiate a copolymerization of iPN with MMA; the copolymer was examined by ^{13}C-NMR with the intention of comparing the number of benzoate end-groups attached to iPN units with the number adjacent to MMA units.

Experimental

iPN was prepared from commercial 2-acetylnaphthalene by the Wittig reaction using triphenylmethylphosphonium bromide with lithium hexamethyldisilazide as the base in dry tetrahydrofuran. After the usual work-up, the product was recrystallized from methanol (melting point 54.5 - 55°C, in agreement with the literature value (8)). Analysis by capillary GC/MS revealed a single component, M^+ of which had m/z 168. Monomeric MMA and toluene were purified by standard procedures; the samples of ^{13}C-AIBN, ^{14}C,^{3}H-BPO and ^{13}C-BPO were those used previously (1,2,9).

Polymerizations were performed under air-free conditions with toluene as diluent; they were monitored dilatometrically and conversions were not greater than 12%. Polymers were precipitated in methanol, purified by two reprecipitations and finally dried in vacuum.

Radioactive materials were assayed using an LKB Wallac "Spectral" 1219 Liquid Scintillation Counter; ^{13}C-NMR spectra were recorded at 100 MHz on a Bruker WH400 instrument using a 10mm probe.

Results and Discussion

The copolymerizations involving iPN were very slow. For a system in which the concentrations of MMA, iPN and AIBN were 3.10, 0.70 and 1 x 10^{-2} mol dm^{-3} respectively, approx. 12% of the monomers had polymerized after 100 hours at 60°C; for a corresponding system free from iPN, that conversion was reached in approx. 1½ hours.

Figure 1 shows parts of the 100MHz spectra of polymers made at 60°C using ^{13}C-AIBN. Spectra (a) and (b) refer respectively to a homopolymer of MMA and a copolymer made from a feed in which $[iPN]/[MMA]$ was 0.23; the peaks result from the methyl carbons in $(CH_3)_2C(CN)-$ end-groups. The two signals in spectrum (a) cover equal areas and they closely resemble those found in a 25MHz spectrum of a similar polymer (10). Spectrum (b) contains additional peaks and resembles that for a copolymer of alpha-methylstyrene with MMA, prepared using the enriched initiator (1). The spectral range 24 to 33 ppm is expected to contain two pairs of signals, one as in spectrum(a)

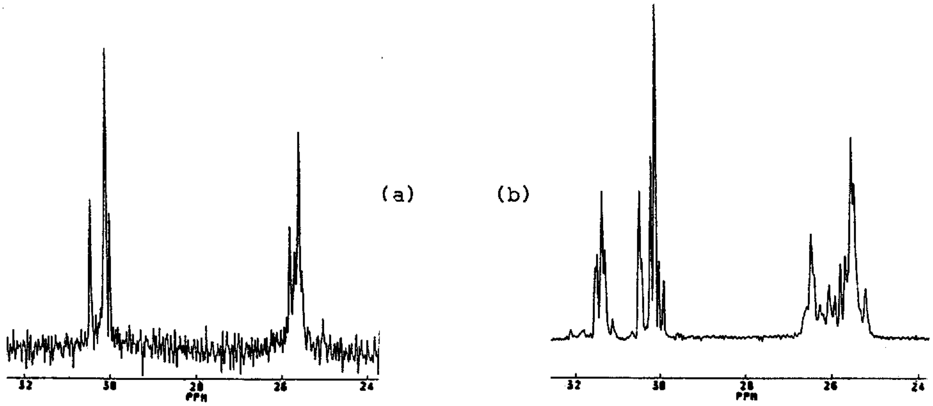

Figure 1. 100MHz ^{13}C-NMR spectra (24 - 32 ppm) of polymers made using azobis(isobutyronitrile) enriched with carbon-13.

(a) homopolymer of MMA (b) copolymer of MMA with iPN.

and the other arising from $(CH_3)_2C(CN)-$ groups attached to iPN units. The signals at ca. 31.5 and 30.2 ppm are resolved and cover areas in the ratio 0.54 : 1; comparison of spectra (a) and (b) indicates that the downfield signal is associated with initiator fragments joined to iPN units and the upfield signal to fragments adjacent to MMA units. The other signals of the two pairs overlap in the neighbourhood of 26 ppm and, as expected, they cover a total area equal to the sum of those corresponding to the resolved downfield signals. From the relationship (I)

$$\frac{\text{no. of } (CH_3)_2C(CN)\text{- adjacent to iPN}}{\text{no. of } (CH_3)_2C(CN)\text{- adjacent to MMA}} = \frac{\text{area for 31.5 ppm peak}}{\text{area for 30.2 ppm peak}}$$

$$= \frac{k_{iPN}[iPN]}{k_{MMA}[MMA]} \qquad \text{(I)}$$

it is found that k_{iPN}/k_{MMA}, i.e. the ratio of the rate constants for the additions of $(CH_3)_2C(CN)\cdot$ to iPN and MMA, is 2.35. The corresponding quantities for 2-vinylnaphthalene (VN) (11), alpha-methylstyrene (MSTY) (1) and styrene (STY) (10) i.e. k_{VN}/k_{MMA}, k_{MSTY}/k_{MMA} and k_{STY}/k_{MMA}, are 2.5, 1.7 and 1.8 respectively.

For a copolymer of iPN with MMA made using ^{14}C,^{3}H-BPO, relationships (II) and (III) are applied (2)

$$\frac{\text{no. of benzoate end-groups}}{\text{sum of nos. of benzoate and phenyl end-groups}} = x$$

$$= \frac{^{14}\text{C-activity of copolymer}}{^{14}\text{C-activity of peroxide}} \times \frac{^{3}\text{H-activity of peroxide}}{^{3}\text{H-activity of copolymer}} \qquad \text{(II)}$$

$$\frac{x}{1 - x} = \frac{k'_{\text{iPN}}[\text{iPN}]}{k_1} + \frac{k'_{\text{MMA}}[\text{MMA}]}{k_1} \qquad \text{(III)}$$

where k_1, k'_{iPN} and k'_{MMA} are respectively the rate constants for the decarboxylation of $C_6H_5.CO.O.$ to give the phenyl radical, the addition of $C_6H_5.CO.O.$ to iPN and the corresponding reaction for MMA. A copolymer was prepared from a system in which the concentrations of iPN, MMA and $^{14}C,^{3}H$-BPO were 0.35, 3.94 and 0.56 x 10^{-2} mol dm^{-3} respectively. The specific activities (in Bq g^{-1}) of the peroxide were 0.83 x 10^{6} (carbon-14) and 1.07 x 10^{6}(tritium) and those of the copolymer were 0.73 x 10^{4} (carbon-14) and 1.25 x 10^{4} (tritium); the values of x and x/(1 - x) are therefore 0.753 and 3.05 respectively. By application of (III) taking k'_{MMA}/k_1 as 0.31 $mol^{-1}dm^{3}$, it is found that k'_{iPN} is 5.2 mol^{-1} dm^{3}; the corresponding quantities for VN (12), MSTY and STY (2) are 5.3, 2.8 and 2.5 respectively. It must be noted that the derived value of k'_{iPN} is rather sensitive to variation in the value of x, found from four specific activities. For the copolymer considered here, a shift in the value of x to 0.74 decreases k'_{iPN}/k_1 to 4.7 $mol^{-1}dm^{3}$; if x is taken as 0.77, k'_{iPN}/k_1 becomes 6.1 $mol^{-1}dm^{3}$.

A copolymer was prepared using BPO enriched with carbon-13, from a system in which [iPN]/[MMA] was 0.11. The benzoate end-groups gave well defined signals in the ^{13}C-NMR spectrum of the copolymer; the spectrum was clearly different from that of an appropriate homopolymer of MMA. There was therefore qualitative evidence for the addition of $C_6H_5.CO.O.$ to iPN but it was not possible to make quantitative studies. The procedure involving ^{13}C-BPO was used successfully, even with 25MHz spectra, to compare the numbers of benzoate groups attached to units from MMA and stilbene (STL) when a mixture of those substances was polymerized (9). The explanation for the failure with the system MMA/iPN is most probably similar to that advanced (9) to account for the failure of the procedure in attempts to compare the reactivities of MMA and STY towards the benzoyloxy radical. When STL is used, the end-groups $C_6H_5CO.O.$MMA- and $C_6H_5.CO.O.$STL- are both attached to long sequences of MMA units, so little STL being incorporated in the chains. When a monomer such as STY or iPN is used with MMA, the product contains comparable numbers of the two types of monomeric units, distributed statistically along the chains; the signals from the initiator fragments are then affected not only by the adjacent monomeric units but also by more remote units so that the spectrum is greatly complicated.

The relative reactivities at 60°C of STY, MSTY, VN and iPN towards the 1-cyano-1-methylethyl radical are 1, 0.9, 1.4 and 1.3 respectively; the corresponding quantities for the monomers with $C_6H_5.CO.O.$ are 1, 1.1, 2.1 and 2.1. The monomers containing naphthyl groups are more reactive than the two styrenes towards both radicals. The effect can be explained in terms of greater stabilization of the product radical, due to the presence of the naphthyl group instead of the phenyl group. It appears that introduction of an α-methyl group into either STY or VN has little effect upon reactivity towards the initiating radicals. This conclusion agrees with that reached for other pairs of monomers $CH_2{:}CHX$ and $CH_2{:}C(CH_3)X$ in reactions with small radicals or with polymer radicals (13). It should be noted however that the polymer radicals derived from $CH_2{:}CHX$ and $CH_2{:}C(CH_3)X$ differ significantly in their reactivities towards monomers, in a sense explicable by steric interference caused by the methyl group.

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