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THE REACTIONS OF BUTADIENE WITH THE 1-CYANO-1-METHYLETHYL AND 1-PHENYLETHYL RADICALS

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Abstract—Butadiene (BD) has been copolymerized with methyl methacrylate (MMA) using as initiator ^{13}C-enriched samples of either azobisisobutyronitrile at 60°C or 1,1′-azobis(1-phenylethane) (APE) at 100°C. The initiator fragments in the copolymers have been examined by ^{13}C-NMR and the numbers attached to units derived from the comonomers have been compared, making allowance for the fact that the BD units may possess 1,2- or 1,4-configurations. The ratio, k_{BD}/k_{MMA}, of the rate constants for the reactions of the initiating radical with the monomers is 1.3 for the 1-phenylethyl radical and 7.0 for the 1-cyano-1-methylethyl radical; the former quantity is consistent with a value of 2.3 for k_{BD}/k_{STY} obtained from the examination of a copolymer of BD with styrene (STY), prepared using APE. The model radical approach is further tested and the reactivities of BD towards the initiating radicals are discussed in terms of its reactivities towards the polySTY and the polymethacrylonitrile radicals. In all the studied systems, most of the BD units adjacent to initiator fragments have the 1,4-structure.

INTRODUCTION

The reactivities of various monomers towards the 1-cyano-1-methylethyl radical [1], the 1-phenylethyl radical [2] and certain other carbon-centred radicals [3, 4] have been compared by a procedure involving study of the end-groups in copolymers. Azo compounds, suitably enriched with carbon-13, are used as sources of the required radicals to initiate copolymerizations carried to low conversions. The resulting copolymers are examined by ^{13}C-NMR and, in most cases, it is possible to separate the signals arising from the initiator fragments attached to the two types of monomeric units. Provided that an adequate pulse delay time is used, the ratio of the two types of end-groups can be found from the ratio of the areas covered by the peaks. The rate constants, k_1 and k_2, for additions of radical R· to the monomers, M_1 and M_2, are compared by means of the relationship

$$\frac{\text{No. of end-groups } R\cdot M_1\text{—}}{\text{No. of end-groups } R\cdot M_2\text{—}} = \frac{k_1[M_1]}{k_2[M_2]} = \frac{A_1}{A_2} \quad (1)$$

in which $[M_1]$ and $[M_2]$ are the concentrations of the monomers in the initial feed and A_1 and A_2 are the spectral areas for the signals from the two types of end-groups. The present publication refers to an extension of these studies to the reactions of butadiene (BD) with the 1-cyano-1-methylethyl and 1-phenylethyl radicals, using methyl methacrylate (MMA) and styrene (STY) as comonomers; the former radical was generated by thermolysis of azobisisobutyronitrile (AIBN) at 60°C and the latter by the thermolysis of 1,1′-azobis(1-phenylethane) (APE) at 100°C.

Part of the interest in the diene lies in the fact that each BD unit adjacent to an initiator fragment could have one of three structures, viz. 1,2-, *cis*-1,4- and *trans*-1,4-. The NMR study might make it possible to determine the relative numbers of initiator fragments attached to these units. The numbers could then be compared with those of the three types of structures for units in the whole polymers and copolymers. The configuration of a particular diene unit is fixed when the next monomeric unit is added and so it might depend upon the nature of the reacting monomer. It is possible also that the configuration could be influenced by the identity of the radical which had previously reacted with the diene. These possibilities might be tested by consideration of the configurations of the diene units adjacent to end-groups of various types in polymers and copolymers of the diene.

A previous comparison of the reactivities of some conjugated dienes (viz. BD, isoprene, 2,3-dimethylbutadiene and chloroprene) with the benzoyloxy radical depended upon the use of radioactively labelled benzoyl peroxide as the initiator of polymerization; the dienes have reactivities generally similar to those of most vinyl monomers [5]. Procedures involving the peroxide either enriched with carbon-13 or radioactively labelled have shown that 1,4-diarylbutadienes are particularly effective in capturing the benzoyloxy radical [6, 7] although they have very

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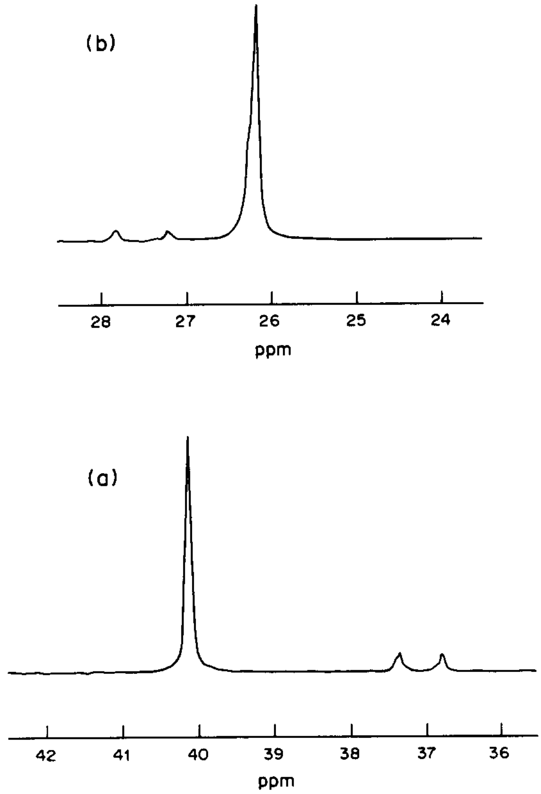

Fig. 1. Parts of the 75 MHz ^{13}C-NMR difference spectra for homopolymers of BD, prepared using ^{13}C-enriched initiators. (a) APE, (b) AIBN.

low reactivities towards the 1-cyano-1-methylethyl radical. The studies with radioactive initiators cannot by themselves provide information on the configurations of the diene units attached to initiator fragments.

EXPERIMENTAL PROCEDURES

Descriptions have been given of the preparation of AIBN enriched with carbon-13 in its methyl groups [1] and of APE in 1-^{13}C-enriched form [8]. Monomers were purified by standard procedures.

Polymerizations were performed under air-free conditions at 60°C in benzene for AIBN and at 100°C in toluene for APE. Total concentrations of monomers were *ca* 30% by volume and initiator concentrations were between 0.2×10^{-2} and 2×10^{-2} mol dm^{-3}. The reactions were monitored by dilatometry and conversions did not exceed 10%. Matching runs with unenriched and ^{13}C-samples of initiator were performed. Polymers were recovered by precipitation in methanol, purified by reprecipitation from benzene solutions and finally dried in vacuum at room temperature.

^{13}C-NMR spectra were recorded for 5–10% solutions of polymers in $CDCl_3$ using first a JEOL FX100 Fourier-transform spectrometer at Lancaster, operating at 25.05 MHz, and then a BRUCKER AM300 spectrometer at Townsville, operating at 75.469 MHz; the two sets of spectra gave similar information and only the 75 MHz spectra are now reported. For each polymer and copolymer of BD, a difference spectrum was obtained by subtracting the spectrum for a polymer made using unenriched initiator from that of the matching polymer prepared with ^{13}C-enriched initiator.

The 75 MHz spectra were recorded with a 54° pulse and delay times of 4 and 8 sec for polymers prepared using AIBN and APE respectively. These delay times are amply sufficient for all signals from the enriched sites in the end-groups to be fully relaxed between acquisitions. The spin-lattice relaxation times of the methyl carbons in $(^{13}CH_3)_2C(CN)$— end-groups in polyMMA are 0.30 and 0.21 sec when measured at 25 MHz [9]; those of the benzylic carbon atoms in $CH_3 \cdot {}^{13}CHPh$— end-groups in STY/acrylonitrile (AN) copolymers are 0.5 ± 0.1 sec, when measured at either 50 or 75 MHz [2]. The corresponding relaxation times, measured at 75 MHz, for 1-cyano-1-methylethyl groups attached to what have been identified as 1,4-BD and 1,2-BD units are 0.65–0.70 and 0.5–0.6 sec respectively; for 1-phenylethyl end-groups joined to 1,4-BD, 1,2-BD and MMA units, they are 1.45–1.50, 1.0–1.40 and <0.70 sec respectively. The signal near 40 ppm, arising from the benzylic carbon atoms in 1-phenylethyl groups attached to 1,4-BD units, has a small component with a value of T_1 significantly less than that quoted.

RESULTS

Figure 1 shows parts of the 75 MHz ^{13}C-NMR difference spectra for samples of polyBD prepared using AIBN or APE; the peaks are due to the isotopically enriched sites in end-groups derived from the initiators. The major peak at 40 ppm in spectrum "a", referring to polymer made using APE, is associated with initiator fragments attached to 1,4-units (*trans* and/or *cis*) and the smaller peaks near 37 ppm to fragments joined to 1,2-units. These assignments are based on three considerations.

(i) For many polymers with a repeat unit —CH_2—CHX— (for a 1,2-BD unit, X is —CH=CH_2), there are two absorptions in the range 36–39 ppm associated with the benzylic carbon atoms in 1-phenylethyl end-groups [2]; the presence of two absorptions is associated with the two stereochemically distinct end-group dyads in such polymers.
(ii) The methine carbon atom in a STY unit in a STY/1,2-BD dyad in a copolymer gives a ^{13}C-NMR adsorption at *ca* 3 ppm higher field than the corresponding absorption for a STY/1,4-BD dyad [10]; in this connection, a 1-phenylethyl end-group with an attached BD unit can be regarded as a STY/BD dyad.
(iii) PolyBD made by radical polymerization consists predominantly of 1,4-units.

Comparison of the areas covered by the peaks in Fig. 1(a) indicates that, for polymerization initiated by APE at 100°C, 84% of the BD units adjacent to 1-phenylethyl end-groups are of the 1,4-type; a separate experiment, involving the use of the 25 MHz spectrometer, yielded a value of 82%. These proportions are very similar to that for all the BD units in a polymer prepared by a free radical process initiated by AIBN [11, 12]. The two spin-lattice relaxation times associated with the peak at 40 ppm are interpreted as showing that the peak consists of two signals, one corresponding to 1-phenylethyl groups attached to *trans* 1,4-BD units and the other to the initiator fragments joined to *cis* 1,4-units.

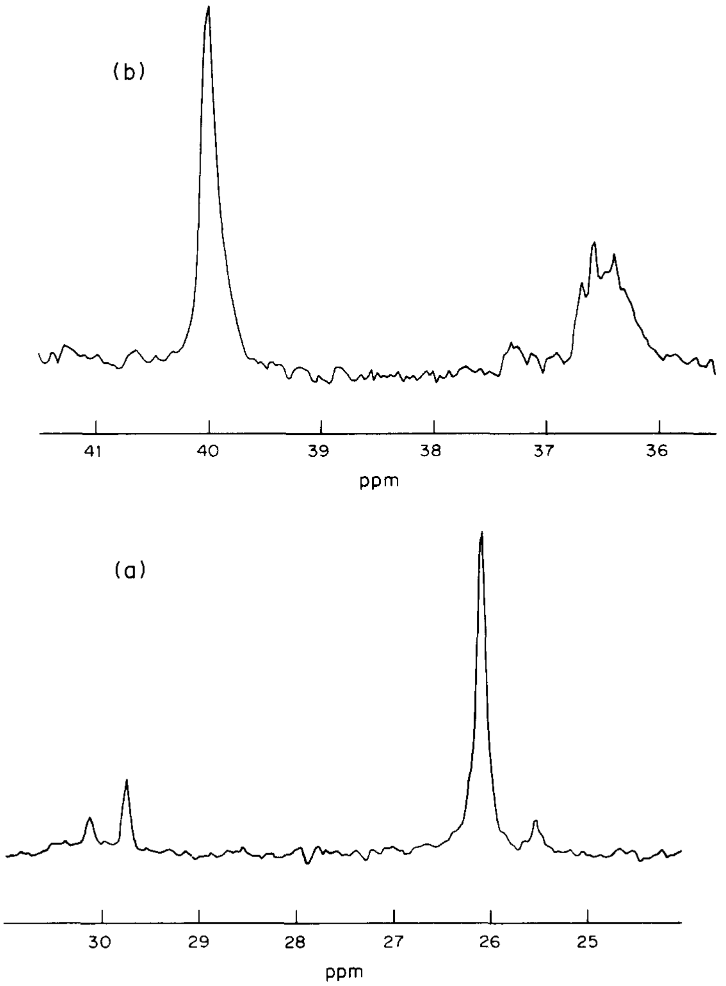

Fig. 2. Parts of the 75 MHz ^{13}C-NMR difference spectra for copolymers of BD with MMA; (a) prepared using ^{13}C-enriched AIBN with [BD]/[MMA] = 0.21; (b) prepared using ^{13}C-enriched APE with [BD]/[MMA] = 1.68.

The two peaks between 27 and 28 ppm in Fig. 1(b) are assigned to the methyl carbon atoms of 1-cyano-1-methylethyl end-groups adjacent to 1,2-BD units. The two methyl signals arising from the initiator fragment in any grouping $(CH_3)_2C(CN)\cdot CH_2\cdot CHX$— are expected to cover equal areas [9]; the two peaks under consideration correspond to approximately equal areas but reliable measurements are not possible because the signals are weak and that at *ca* 27.1 ppm is close to a resonance associated with repeat units of the polymer. The prominent peak at *ca* 26 ppm is connected with initiator fragments joined to 1,4-BD units; a shoulder is evident on this peak and another spectrum provided clear evidence for splitting of the peak into two components probably because of the occurrence of *cis* and *trans* forms of the 1,4-units. Integration of the peaks between 27 and 28 ppm and that at 26 ppm shows that 92% of the BD units adjacent to 1-cyano-1-methylethyl groups in the polymer are of the 1,4-type. The errors in the determinations of the relative numbers of 1,4- and 1,2-units adjacent to the chain-ends are likely to be quite large but it is clear that the 1,4-units greatly outnumber the 1,2-units, more so for the polymers prepared at 60°C with AIBN than those made at 100°C with APE.

Figure 2(a) shows part of the ^{13}C-NMR difference spectrum for a typical copolymer of MMA with BD, prepared using AIBN as initiator in a feed for which [BD]/[MMA] was 0.21. The peaks at *ca* 30 ppm (area A') arise from methyl groups in initiator fragments adjacent to MMA units; these groups are expected to produce another signal, also covering an area A', at *ca* 26 ppm [1]. The peaks between *ca* 25 and 28 ppm (total area, A'') also include those corresponding to end-groups $(CH_3)_2C(CN)\cdot$1,2-BD— and $(CH_3)_2C(CN)\cdot$1,4-BD—; comparison with Fig. 1(b) indicates that the groupings containing 1,2-units give rise to a pair of resonances between *ca* 27 and 28 ppm and that those containing 1,4-units give a signal close to 26 ppm. If A_{MMA} and A_{BD} are the total areas for signals due to initiator fragments joined to MMA and BD units respectively, then

$$\frac{A_{BD}}{A_{MMA}} = \frac{A'' - A'}{2A'}. \qquad (2)$$

For the copolymer referred to in Fig. 2(a), A''/A' is 3.4 so that A_{BD}/A_{MMA} is 1.2. For copolymers prepared similarly but from systems in which [BD]/[MMA] had values of 0.35 and 0.14, the value of A''/A' are 6.0 and 2.5 and so those of A_{BD}/A_{MMA} are 2.5 and 0.75 respectively.

The ^{13}C-NMR difference spectrum in Fig. 2(b) refers to a copolymer derived from a system in which [BD]/[MMA] was 1.68 and APE was present as initiator. The peak at 40 ppm (area, A''') is associated with initiator fragments attached to 1,4-BD units. The signals between 35.5 and 38 ppm (total area A'''') correspond to initiator fragments attached either to 1,2-BD or to MMA units. It is supposed that 84% of the diene units adjacent to initiator fragments have the 1,4-structure, i.e. the same proportions as for the homopolymer of BD. On this basis, A'''' includes a contribution of $0.19A'''$ due to initiator fragments attached to 1,2-BD units, so that

$$\frac{A_{BD}}{A_{MMA}} = \frac{1.19A'''}{A'''' - 0.19A'''}. \tag{3}$$

The modifications to A''' and A'''' to give A_{BD}/A_{MMA} conform to the view that, in Fig. 2(b), the peaks near 37.2 and 36.5 ppm correspond to structures in which initiator fragments are joined to 1,2-BD and MMA units respectively. For the copolymer referred to in Fig. 2(b), A'''/A'''' is 1.35 so that A_{BD}/A_{MMA} is 2.2. For a copolymer derived from a system in which [BD]/[MMA] was 0.37, A'''/A'''' is 0.26 and so it is deduced that A_{BD}/A_{MMA} is 0.33.

Figure 3 shows plots of A_{BD}/A_{MMA} vs [BD]/[MMA] for systems involving either AIBN or APE. From the slopes of the lines and using equation (1), k_{BD}/k_{MMA} is found to be 1.3 for the 1-phenylethyl radical at 100°C and 7.0 for the 1-cyano-1-methylethyl radical at 60°C.

Copolymers of BD with STY were prepared using [BD]/[STY] at 1.02 with APE either unenriched or containing carbon-13; the ^{13}C-NMR difference spectrum is shown in Fig. 4. The peak at 40 ppm (relative area, 1.0) corresponds to 1-phenylethyl groups attached to 1,4-BD units. Signals for the end-groups joined to 1,2-BD units and those joined to STY units are almost coincident and give two peaks near 37 ppm (relative area, 0.8). It is assumed again that 16% of the BD units adjacent to initiator fragments have the 1,2-structure; application of equations similar to (3) and (1) leads to values of 2.3 for both A_{BD}/A_{STY} and k_{BD}/k_{STY}. It is known [2] that, for reactions with the 1-phenylethyl radical at 100°C, k_{STY}/k_{MMA} is 0.53 and so the value found for k_{BD}/k_{STY} corresponds to 1.2 for k_{BD}/k_{MMA}, in agreement with that obtained by direct study of copolymers of BD with MMA.

DISCUSSION

In a previous publication [2], it was shown that the relative rate constants for the reactions of monomers with the 1-phenylethyl radical agree quite well with the relative rate constants for the reactions of the monomers with the polySTY radical, as deduced from monomer reactivity ratios for copolymerizations of the monomers with STY. This agreement suggests that the small radical is a good model for the polymer radical in respect of selectivity in reactions with many monomers; exceptions seem to arise for monomers which display or might well be expected to display significant penultimate group effects in copolymerizations and for monomers known to have rather low ceiling temperatures [13]. For the radical copolymerization of STY (monomer-1) with MMA, the monomer reactivity ratio r_1 is close to 0.5 so that k_{MMA}/k_{STY} for reactions of the monomers with the polySTY radical can be taken as two. Greenley's [14] recalculations of data for the copolymerization of STY (monomer-1) with BD give values of 0.33 and 0.84 for r_1, corresponding to values of 3.0 and 1.2 for k_{BD}/k_{STY} and leading to values of k_{BD}/k_{MMA} of 1.5 and 0.6 for reactions with the polySTY radical; the higher of these values is quite close to the value of 1.3 now reported for k_{BD}/k_{MMA} in reactions of the monomers with the 1-phenylethyl radical.

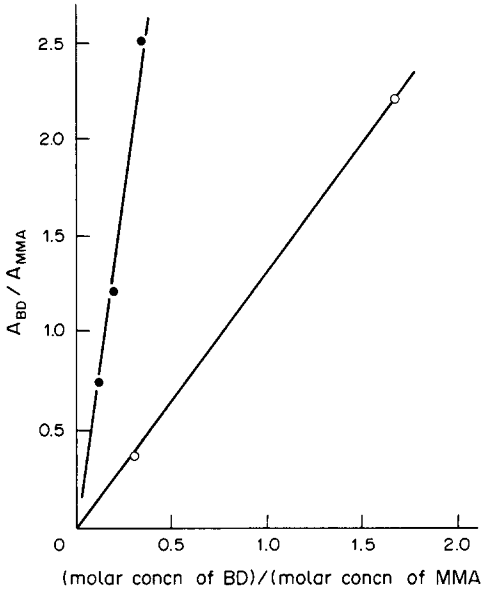

Fig. 3. Plots of (area covered by peaks due to enriched sites in initiator fragments attached to BD units)/(corresponding quantity for fragments attached to MMA units) vs [BD]/[MMA] in initial feed for copolymerization. ○, APE; ●, AIBN.

According to the model radical approach, the rate constants for reactions of monomers with the 1-cyano-1-methylethyl radical should correlate with those for their reactions with the polymethyacrylonitrile radical, as found from studies of copolymerizations with methacrylonitrile (MAN); this correlation has been confirmed for several monomers [1] and BD can now be tested from this point of view. Walling's compilation [15] gives k_{BD}/k_{MMA} as *ca* 17 for reactions with the polyMAN radical whereas a value of 7.0 is now found for reactions with the 1-cyano-1-methylethyl radical. The reactivities of monomers towards the polyMAN radical were based upon terminal models for the copolymerizations. It has been shown convincingly that a penultimate model is much more satisfactory when dealing with copolymerizations of STY with AN [4, 16, 17]. This point can be illustrated by noting that the value of k_{STY}/k_{AN} for reactions with the 1-phenylethyl radical is 0.20 whereas for reaction with the polySTY radical it is 0.33 according to a terminal model for the copoly-

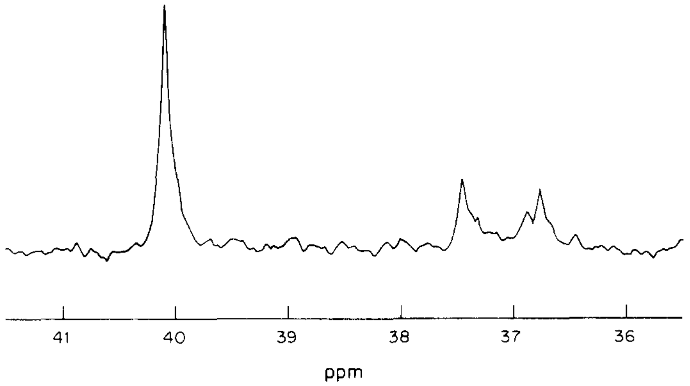

Fig. 4. Part of the 75 MHz ^{13}C-NMR difference spectrum for a copolymer of BD with STY, prepared using ^{13}C-enriched APE with [BD]/[STY] = 1.02.

merizations of STY with AN [4, 16, 17]. This point can be illustrated by noting that the value of k_{STY}/k_{AN} for reactions with the 1-phenylethyl radical is 0.20 whereas for reaction with the polySTY radical it is 0.33 according to a terminal model for the copolymerization STY/AN; the difference between the two values of k_{STY}/k_{AN} suggests that the model radical approach is not very satisfactory in this case. If however the penultimate model is used for the copolymerization, the values of k_{STY}/k_{AN} for reactions with polymer radicals represented as P·STY·STY· and P·AN·STY· are 0.23 and 0.63 respectively; these values agree with those found for reactions with the 1,3-diphenylpropyl and 3-cyano-1-phenyl radicals [4]. It is quite possible that similar considerations might apply to systems involving MAN but the information required for a test seems at present not to be available.

Foster and Binder [18] reported that the proportion of 1,4-BD units increased as various comonomers were introduced into polymers of BD made by radical reactions. Other workers found no change in the relative numbers of 1,2- and 1,4-units in copolymers BD/STY [19, 20] and BD/MMA [21] as the content of comonomer was increased, in the case of MMA up to *ca* 80 mol%. In the present work, it has not been possible to detect with any certainty an influence of the nature of the monomer (M) on the configuration adopted by the diene unit produced by reactions of the radicals $(CH_3)_2C(CN)\cdot BD\cdot$ and $CH_3\cdot CH(Ph)\cdot BD\cdot$ with M (BD, MMA or STY). This failure is not surprising since very low proportions of BD for the copolymerizations BD/MMA and BD/STY could not be used because few of the initiating radicals would then have been captured by the diene. Under these circumstances, the concentrations of BD actually used make it inevitable that many of the radicals formed by the reaction of an initiating radical with BD will themselves react with BD. It must be concluded that, if the nature of M influences the configuration of the BD unit adjacent to an initiator fragment, the effect is not large.

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