Endgroups in Copolymers of Acenaphthylene with Methyl Methacrylate Prepared with Azoisobutyronitrile as Initiator

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ABSTRACT

Copolymers of acenaphthylene (ACN) with methyl methacrylate (MMA) have been prepared with azobis(isobutyronitrile-β,β-$^{13}C_2$) as initiator. The endgroups derived from the initiator have been examined by ^{13}C-NMR spectroscopy; those attached to ACN units have been distinguished from those attached to MMA units and quantitative comparisons of their numbers have been made. It has been deduced that at 60°C ACN is four times as reactive as MMA toward the $(CH_3)_2C(CN)^{\cdot}$ radical. The marked preference for initiation involving ACN means that, for all copolymers, the ratio of ACN to MMA is appreciably greater for the sites adjacent to the $(CH_3)_2C(CN)-$ endgroups than for the whole copolymer.

Although many 1,2-disubstituted ethylenes engage readily in co-polymerizations, generally their homopolymerizations are very slow; a notable exception is acenaphthylene (ACN) which is reactive in addition polymerizations by radical and other mechanisms. The high reactivity of this monomer [1] and its large heat of polymerization [2] have been attributed to the existence of considerable strain in the

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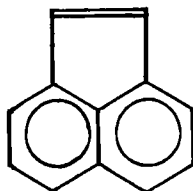
five-membered ring, partially relieved on conversion of the double bond to a single bond. It is significant also that the radical polymerization of ACN in solution is accelerated by high pressures to a much smaller extent than the similar polymerizations of other monomers [3].

The values of the monomer reactivity ratios [1, 4] for radical copolymerizations involving ACN (monomer 1) show that the monomer has high reactivity toward polymer radicals of many types, values of r_1 generally being appreciably greater than unity and those of r_2 being less than 0.5. We now report a study of the reactivity of ACN toward a small initiating radical, viz., 2-cyano-2-propyl, formed by thermolysis of azobis(isobutyronitrile) (AIBN). For this purpose we have used AIBN enriched in its methyl groups with carbon-13 (^{13}C-AIBN) to initiate copolymerizations of ACN with methyl methacrylate (MMA); ^{13}C-NMR spectroscopy has then been used to compare the numbers of initiator fragments attached to ACN and MMA monomeric units. The procedure has been applied previously in investigations of the endgroups in other copolymers, leading to comparisons of the reactivities of various monomers toward the $(CH_3)_2C(CN)^{\cdot}$ radical [5, 6].

Polymers and copolymers of ACN are interesting from several points of view. Copolymers with divinylbenzene have been used for the preparation of ion-exchange resins [7] and more recently of polymer-supported reagents [8]. Polymers and copolymers, commonly with MMA, have been examined in photochemical and photophysical studies [9, 10]; for work of this type it may be important to have detailed information about the endgroups of the macromolecules and also about the monomeric units in their close proximity.

EXPERIMENTAL

ACN (Lancaster Synthesis Ltd.) was recrystallized twice from methanol; MMA and benzene (used as diluent in polymerizations) were purified by standard procedures. ^{13}C-AIBN was prepared from 1,3-^{13}C-acetone (BOC Ltd.); the isotopic abundance of ^{13}C in the methyl groups of the final product was close to 20%.

Polymerizations were performed in the absence of air at 60°C in dilatometers. The reaction mixtures contained ~60% by volume of benzene; concentrations of AIBN were in the region of 2 g/L. There were no inhibition periods for the reactions, and contraction vs time plots were linear. Conversions were kept well below 7%. Polymers

were recovered by precipitation in methanol, purified by reprecipitation from benzene solutions, and finally dried in vacuum at 50°C.

^{13}C-NMR spectra were recorded at ambient temperature using a JEOL FX100 Fourier-transform spectrometer operating at 25.05 MHz. Polymers and copolymers were examined in CDCl$_3$ solution ($\sim$100 mg in 2.2 mL). Spectra, 5000 Hz (200 ppm) in width, were accumulated into 8K data points and zero-filled to 16K data points before Fourier transformation with an exponential weighting function introducing 0.7 Hz line broadening. The pulse repetition time was 1.0 s with a tip angle of 54°. Chemical shifts were referenced to the central CDCl$_3$ resonance at 76.9δ.

RESULTS

Figure 1 refers to the ^{13}C-NMR spectra of homopolymers of ACN and MMA prepared using ^{13}C-AIBN and also a homopolymer of ACN prepared using unenriched AIBN. The $(CH_3)_2 C(CN)-$ endgroups give rise to two separate and equal methyl resonances (25.55 and 30.15δ) for polyMMA; for polyACN they give a set of unresolved resonances (between 22 and 28δ) including fine structure. The resonances associated with ACN monomeric units are considerably broader than those for MMA units whereas the endgroup resonances for the two types of homopolymer are comparable in sharpness. This difference between the spectra for the polymers can be ascribed to the greater chain rigidity in polyACN.

Copolymers of ACN with MMA were prepared as indicated in Table 1; their NMR spectra are shown in Fig. 2. The resonances for initiator fragments are readily identified; the signals for $(CH_3)_2 C(CN)-$ groups attached to MMA units (referred to as R.MMA-) overlap to some extent those for the groups attached to ACN units (referred to as R.ACN-) but the downfield resonance for R.MMA- at 30.25δ is completely resolved although its shape depends upon the overall composition of the copolymer. It is possible to compare the total areas corresponding to the signals for R.MMA- and R.ACN-, and then to compare the numbers of these endgroups from the area (A) of the resolved downfield resonance and that of the overlapping upfield signals (B) using the relationship

$$\frac{\text{no. of R.ACN- groups}}{\text{no. of R.MMA- groups}} = \frac{B - A}{2A} \tag{1}$$

If k_a and k_m are the velocity constants for the competing initiation processes by which $(CH_3)_2 C(CN)^\cdot$ radicals become attached to the monomers ACN and MMA, respectively,
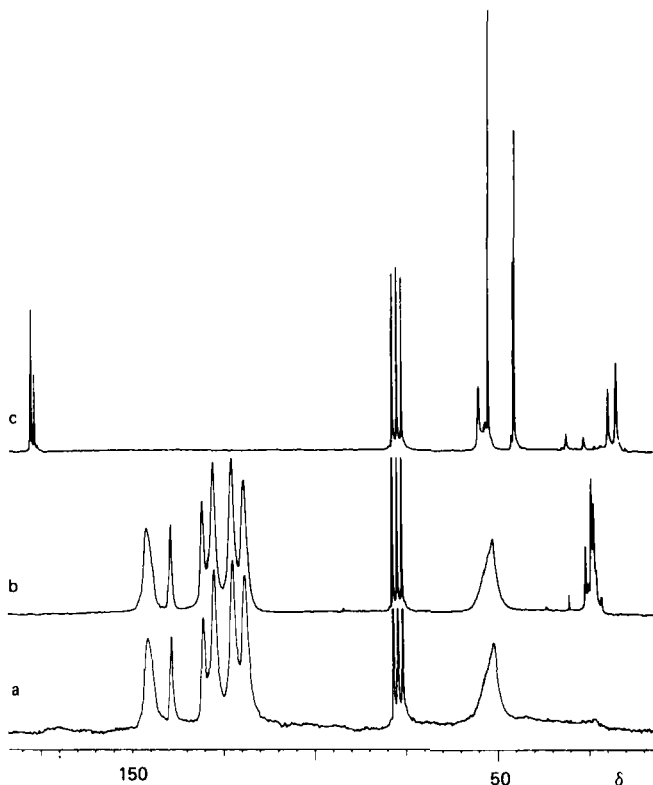
FIG. 1. ^{13}C-NMR spectra for (a) poly-ACN prepared using unenriched AIBN (b) poly-ACN prepared using ^{13}C-AIBN, and (c) poly-MMA prepared using ^{13}C-AIBN. Resonances associated with (i) combined initiator fragments in poly-ACN at 22-28δ, (ii) monomeric units in poly-ACN at ~50 and 115 to 150δ, and (iii) monomeric units in poly-MMA at 45 to 60δ.

$$\frac{B - A}{2A} = \frac{k_a[ACN]}{k_m[MMA]}$$

where [ACN] and [MMA] are the concentrations in the feed.

The values of (B - A)/2A are 1.33 and 0.52, respectively, for Copolymers 2 and 3; the derived values of k_a/k_m are 3.7 and 4.2, respectively. It is apparent that ACN is about 4 times as reactive as MMA toward the $(CH_3)_2C(CH)^{\cdot}$ radical at 60°C.

TABLE 1. Copolymers of Acenaphthylene (ACN) with Methyl Methacrylate (MMA)

Copolymer	Initial [ACN]/[MMA] in feed	Total weight (g) of monomers	Weight (g) of copolymer	[ACN]/[MMA] in copolymer[b]	
				Calc[c]	Calc[d]
1[a]	0.39	4.50	0.17	0.88	0.71
2	0.37	4.67	0.18	0.84	0.68
3	0.12	5.16	0.26	0.27	0.27

[a]AIBN not enriched with carbon-13.
[b]Calculated on the basis of initial feed.
[c]$r_1 = 2.26$, $r_2 = 0.44$ (Ref. 4).
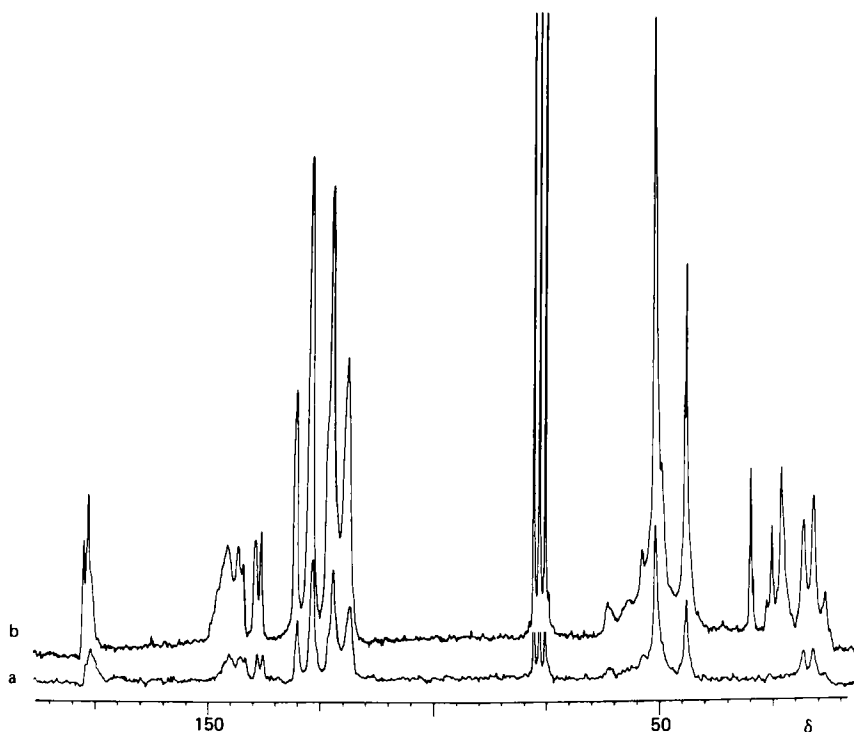[d]$r_1 = 1.05$, $r_2 = 0.38$ (Ref. 1).

FIG. 2. ^{13}C-NMR spectra for copolymers of ACN with MMA (see Table 1).   (a) Copolymer 1 (unenriched AIBN).   (b) Copolymer 2 (^{13}C-AIBN).

DISCUSSION

In the copolymerization of ACN with MMA, there is preferential consumption of ACN so that errors arise from using initial values of [ACN]/[MMA] in calculations based on measurements on copolymers recovered after finite conversions; the conversions were, however, low so that the changes in feed composition were small. Errors from this source can be neglected, being considerably smaller than in the case of vinyl chloride with MMA where they were appreciable although not large [6].

Combining the results now reported with those presented previously [5, 6], it is found that the relative reactivities toward the radical $(CH_3)_2 C(CN)°$ of ACN, styrene, MMA, methacrylonitrile, and vinyl chloride are 4, 1.8, 1.0 (standard), 0.6, and 0.07, respectively; these figures refer to 60°C except in the case of vinyl chloride for which the comparison is based on copolymerizations with MMA at 45°C.
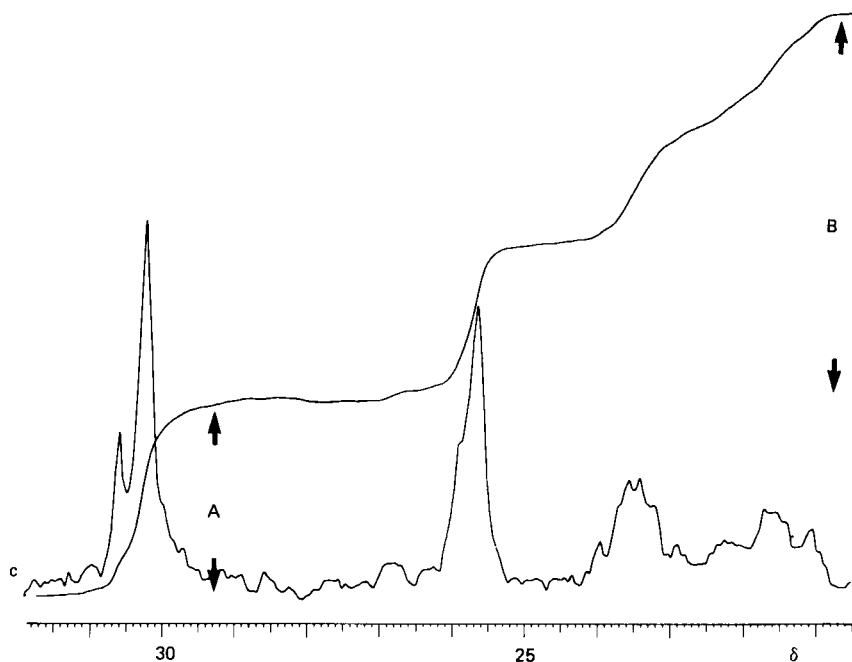
FIG. 2. (continued) (c) Copolymer 3 (^{13}C-AIBN), showing detail of endgroup resonances.

For Copolymers 2 and 3, the ratios of ACN to MMA units at the sites adjacent to $(CH_3)_2 C(CN)-$ groups are 1.33 and 0.52, respectively; these values are considerably greater than the corresponding ratios for the whole copolymers (see Table 1). The pronounced tendency for concentration of ACN units near the initiator fragments in the copolymers is found over the whole range of copolymer compositions, as illustrated in Fig. 3 where the calculated values of (no. of R.ACN–groups)/(sum of nos. of R.ACN– and R.MMA– groups) are plotted against the mole fractions of ACN units in the whole copolymers calculated taking $r_1 = 2.0$ and $r_2 = 0.4$; in all cases the calculations refer to systems for which there are negligible changes in [ACN]/[MMA] in the feeds.

It is usually supposed that, for most monomers, attack of radicals occurs almost exclusively at the methylene groups (tail addition). Radical trapping experiments [11, 12] have confirmed that addition of this type is dominant in the reaction of benzoyloxy radicals with com-
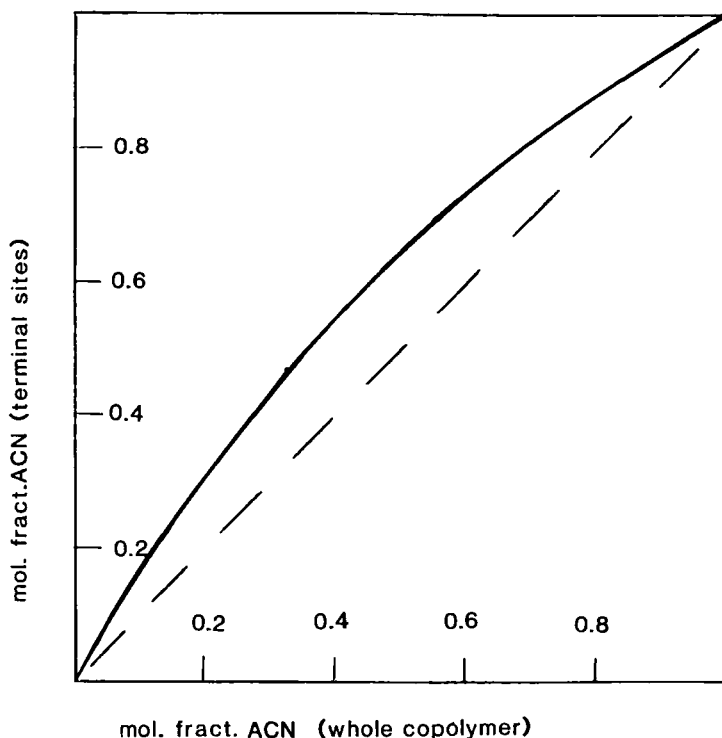
FIG. 3. Plot showing tendency for ACN units to be concentrated at sites adjacent to $(CH_3)_2 C(CN)$ endgroups in ACN/MMA copolymers. Composition of whole copolymer calculated from initial composition of feed with $r_1 = 2.0$ and $r_2 = 0.4$. Mole fraction of ACN at terminal sites (full line) calculated on basis of ACN being four times as reactive as MMA toward the initiating radical.

mon monomers although head addition can be detected and is indeed quite pronounced for vinyl acetate. It was further shown that phenyl and tert-butoxy radicals are more selective in their reactions with monomers, showing very great preference for tail addition. Conclusions about the reaction of the $C_6H_5.CO.O^{\cdot}$ radical with styrene have been largely confirmed by NMR studies of endgroups in polymers prepared using as initiator benzoyl peroxide enriched in [13]. There is no evidence that head addition is appreciable for the $(CH_3)_2 C(CN)^{\cdot}$ radical; NMR examination of polymers prepared using samples of AIBN isotopically enriched with ^{13}C, ^{15}N, or ^{2}H gave no indication of the presence in the polymers of more than one type of endgroup derived from the initiator [14]. For a symmetrically substituted monomer such as ACN, the question of head and tail additions does not arise.

In this connection it should be noted that the molecule of ACN has two sites of equal reactivity whereas the molecule of MMA has one site of high reactivity (leading to tail addition) and another of very much lower reactivity (leading to head addition). When comparing the reactivity of ACN with that of a monomer such as MMA toward an initiating radical, it may be necessary to regard the effective concentration of ACN as double its molar concentration; of course, reaction of one of the sites of a particular molecule of ACN immediately renders the other site in that molecule unavailable for initiation. It is also important to note that a solution of a monomer such as ACN contains pairs of reactive sites; for this reason the distribution of sites differs significantly from that in a dilute solution of, say, MMA where they normally occur singly.

The use of ^{13}C-AIBN enriched in its methyl groups is particularly well suited for the study by NMR of endgroups in copolymers containing monomeric units with chiral sites. The endgroups in a binary copolymer of this type give two pairs of equal resonances although in practice there may be some overlap; provided that one of the four signals can be resolved, the areas corresponding to the two types of endgroups can be determined and the numbers of these groups can be compared (see Eq. 1). MMA is especially useful as a reference monomer in these investigations because the two signals due to the R.MMA-endgroups are well separated.

The advantages associated with the twin signals from endgroups derived from azobis(isobutyronitrile-β,β-^{13}C$_2$) (β,β-^{13}C-AIBN), as used in this work, would be absent if use were made of azobis(isobutyronitrile-α-^{13}C) (α-^{13}C-AIBN) which would give $(CH_3)_2 C(CN)^{\cdot}$ radicals with only the central carbon enriched. There is another reason also for preferring β,β-^{13}C-AIBN to α-^{13}C-AIBN. It is normal experimental practice to generate ^{13}C-NMR spectra using proton noise-decoupling to remove all spin-spin coupling due to interaction with protons; signals for carbon atoms bearing directly bound protons then have increased intensities due to nuclear Overhauser enhancement. Signals for quaternary carbons normally do not gain appreciably in intensity from Overhauser effects. It is found that, for equal numbers of protonated and nonprotonated carbon atoms, signals from the former are normally approximately three times as intense as those from the latter. The monolabeled α-^{13}C-AIBN has the carbon atom reporting on the attached monomeric unit one bond closer to that unit; perturbation of chemical shift due to type and sterochemistry of proximate monomeric units may therefore be enhanced relative to those observed for the methyl resonances of β,β-^{13}C-AIBN. The various considerations referred to in this paragraph make it clear that AIBN enriched with ^{13}C in the CN groups is likely to be less useful than the other types of enriched initiator.

It is interesting to consider the possible use in copolymerizations of other initiators enriched with ^{13}C; many ^{13}C-compounds are available so that synthesis of suitably enriched initiators is feasible. In the case of benzoyl peroxide it would be instructive to compare results

obtained using ^{13}C-peroxide with those already obtained from work involving the peroxide labeled with the radioactive isotopes ^{14}C or ^{3}H [15]. In some preliminary work [16], polymers and copolymers were prepared using benzoyl-carbonyl-^{13}C-peroxide and examined by NMR spectroscopy. The chemical shifts for the signals due to benzoyloxy endgroups attached to polystyrene chains (166.15 and 166.05δ) were different from those for the same endgroups in polyMMA (165.80 and 165.65δ); however, benzoyloxy endgroups in copolymers of styrene with MMA gave single unresolved peaks (about 166.1δ). It is not possible at present to use this method for comparisons of the numbers of benzoyloxy endgroups attached to styrene and MMA units in copolymers. The point made in the preceding paragraph about Overhauser enhancement applies also to the benzoyloxy endgroups derived from benzoyl-carbonyl-^{13}C-peroxide.

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