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END-GROUPS IN POLYMERS AND COPOLYMERS OF ETHYL ACRYLATE PREPARED USING AZOISOBUTYRONITRILE AS INITIATOR

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Abstract—Samples of azoisobutyronitrile enriched with carbon-13 or deuterium have been used for NMR studies of the initiator fragments incorporated in polymers of ethyl acrylate and copolymers of that monomer with styrene. It has been deduced that at 60° styrene is 3.3 times as reactive as ethyl acrylate towards the 2-cyano-2-propyl radical.

INTRODUCTION

Reports have been published [1–3] on the application of NMR spectroscopy to the study of the end-groups in various polymers and copolymers prepared using as initiator azoisobutyronitrile enriched with carbon-13 in its methyl groups ([^{13}C]AIBN). End-group analysis by this technique offers such specificity that, for binary copolymers, it is usually possible to distinguish between initiator fragments attached to the two types of monomer unit; the sensitivity however is inferior to that achievable by radioactive techniques involving AIBN labelled with either carbon-14 or tritium. When using [^{13}C]AIBN, it is necessary to choose conditions for the polymerization to give polymer of fairly low molecular weight so that the content of end-groups derived from the initiator is comparatively high, usually not less than one such group for about 1500 monomeric units if the methyl groups are enriched to about 25% carbon-13.

Deuterated AIBN ([^{2}H]AIBN) has been used in studies of the decomposition of the azonitrile [4, 5] and in ^{2}H-NMR studies of end-groups which have also been examined by means of ^{15}N-NMR using AIBN enriched with nitrogen-15 in the nitrile groups ([^{15}N]AIBN) [6]. It appears that [^{15}N]AIBN is of value for examination of end-groups only in rather special cases but that the use of [^{2}H]AIBN might offer some general advantages. The natural abundance of deuterium is very much less than that of carbon-13 so that the NMR signals for ^{2}H-enriched groups in a polymer are less affected by the "background", due to the remainder of the polymer molecule, than those for ^{13}C-enriched groups. Further, the preparation of AIBN with a deuterium content of essentially 100%, using d^6-acetone as starting material, is much cheaper than that of AIBN with about 25% abundance of carbon-13 in the methyl groups, starting with [^{13}C]acetone. It has been pointed out [3] that enrichment with carbon-13 in the nitrile groups or at the α-carbon atom is likely to be less useful than enrichment in the methyl groups.

The NMR study of end-groups derived from AIBN has now been extended to polymers and copolymers of ethyl acrylate (EA). Samples of initiator containing carbon-14, carbon-13 or deuterium have been used. It has been possible to overcome various difficulties and to compare the reactivities of styrene (ST) and EA towards the 2-cyano-2-propyl radical.

EXPERIMENTAL

Standard procedures were used for purification of materials, preparation of polymers and copolymers, and examination of products. The preparations and characterizations of isotopically enriched samples of AIBN have been described [1, 6]. Polymerizations were performed at 60° in vacuum dilatometers with benzene as diluent; conversions were restricted to 10%. Polymers and copolymers were recovered by precipitation in hexane and purified by reprecipitation. Rates of polymerization were calculated from rates of contraction. For homopolymerizations of EA, 19.60% contraction was taken as corresponding to 100% polymerization; for copolymerizations of EA and ST, no quantitative use is made of rates of polymerization but it was supposed that the contraction was intermediate between those for the homopolymerizations and that it varied linearly with the composition of the copolymer being produced.

Materials labelled with carbon-14 were assayed by scintillation counting in solution using a twin-channel counter (ICN, Tracerlab). NMR spectra were recorded on a JEOL FX100 Fourier-transform spectrometer, operating at 25.05 MHz for carbon-13 and 15.29 MHz for deuterium; details of the procedures have been given [1, 3]. For examination of polymers and copolymers by gel permeation chromatography, a Waters 502 instrument was used; it was calibrated with polyST standards and the molecular weights quoted are regarded only as approximate.

RESULTS AND DISCUSSION

Table 1 refers to the polymerizations and copolymerizations involving EA. The kinetic chains in radical polymerizations of this monomer are rather long so that the contents of initiator fragments in the polymers are low and the end-group analyses are difficult; the copolymers with ST are of lower molecular weight and therefore are richer in end-groups.

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Table 1. Polymerizations and copolymerizations involving ethyl acrylate

	Type of azonitrile and concn (g/l)	Concn of EA (mol/l)	Concn of styrene (mol/l)	$10^5 \times R_p$ (mol/l/s)	[Styrene]/[EA] in copolymer	$\bar{M}_n \times 10^{-3}$*
PEA-1	^{14}C:1.06	4.23	0	24.90	—	558
PEA-2	^{13}C:1.06	4.23	0	20.20	—	645
PEA-3	^{13}C:2.16	2.12	0	38.70	—	313
PEA-4	^{2}H:1.93	2.12	0	33.00	—	310
PEA-5	^{2}H:1.02	2.12	2.10	2.89	1.50	48
PEA-6	^{2}H:1.04	3.17	1.05	2.52	0.76	90
PEA-7	^{13}C:1.14	1.10	3.14	2.82	3.35	74
PEA-8	^{13}C:0.99	2.12	2.10	2.97	1.49	94
PEA-9	^{13}C:0.96	3.30	1.05	3.96	0.75	99

*Values for $\bar{M}_n$ found from direct comparison with polyST standards without correction.

Comparison of the specific activities of the sample of [^{14}C]AIBN and the derived homopolymer PEA-1 shows that the polymer contained one $(CH_3)_2C(CN)$-end-group for 2600 monomeric units; from this result and the observed rate of polymerization, the rate of incorporation of initiator fragments in the polymer is 0.96×10^{-7} mol l^{-1} sec^{-1}, a value quite close to that for ST under comparable conditions [7]. Estimates by GPC indicated that the number-average degree of polymerization for PEA-1 was about 5600; this result is consistent with that of the end-group analysis if each polymer molecule contained approximately two initiator fragments, as would be the case if termination by combination had been dominant and if transfer reactions with monomer and diluent had not been pronounced.

The ^{13}C-NMR spectrum of PEA-2, made under the same conditions as PEA-1 but with [^{13}C]AIBN, contained no peaks attributable to $(^{13}CH_3)_2C(CN)$- end-groups. Figure 1 shows part of the ^{13}C-NMR spectrum of PEA-3, the molecular weight of which was less than that of PEA-2; the small peak at 26.6δ is assigned to end-groups derived from the azonitrile. The peak is not found in the spectrum of a polymer prepared using unenriched AIBN and occurs in the region where there are signals for $(^{13}CH_3)_2C(CN)$-groups in other polymers; there was no interference from occluded initiator which, if present, would have given a signal at 25.05δ. Comparison of the GPC results for PEA-1 and PEA-3 indicates that the latter polymer contained one initiator fragment for approx. 1500 monomeric units so that detection of the end-groups by ^{13}C-NMR was just possible. The ^{13}C-end-groups in polyEA are expected to give rise to a pair of equal signals because of the presence in the monomeric unit of a chiral site; evidently the separation between the signals is less than for other polymers so that they are not resolved. The NMR spectrum gives no evidence for the existence of two types of end-group derived from the initiator.

PEA-4 was prepared under conditions closely similar to those for PEA-3 but with [^{2}H]AIBN. The rates of decomposition at 60° of unenriched AIBN and [^{2}H]AIBN in dilute solution in benzene were measured by following the consumption of diphenylpicrylhydrazyl [8]. It was found that the two types of AIBN dissociated at very similar rates, that for [^{2}H]AIBN being the smaller by about 10%. The ^{2}H-NMR spectrum of PEA-4 (Fig. 2) contained a single peak at 1.30δ attributed to $(CD_3)_2C(CN)$- end-groups, close to a sharp peak due to occluded

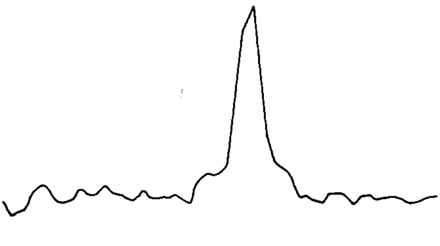

Fig. 1. Part of the ^{13}C-NMR spectrum of polymer PEA-3. The peak at *ca* 26.6δ is attributed to $(^{13}CH_3)_2C(CN)$-end-groups.

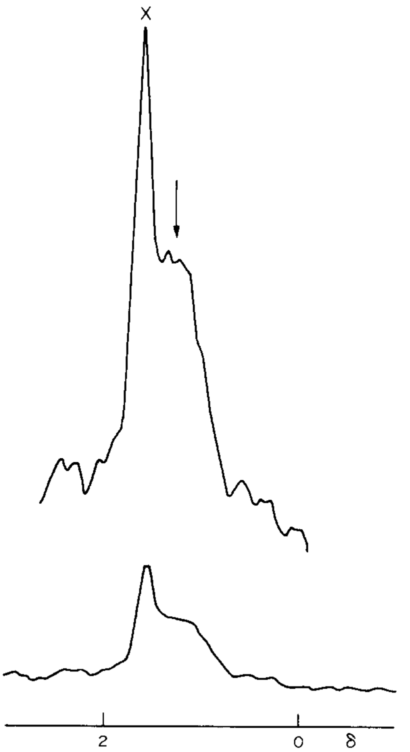

Fig. 2. Part of the ^{2}H-NMR spectrum of polymer PEA-4. The broad peak marked with an arrow is attributed to $(CD_3)_2C(CN)$- end-groups; the peak marked X is due to occluded initiator.

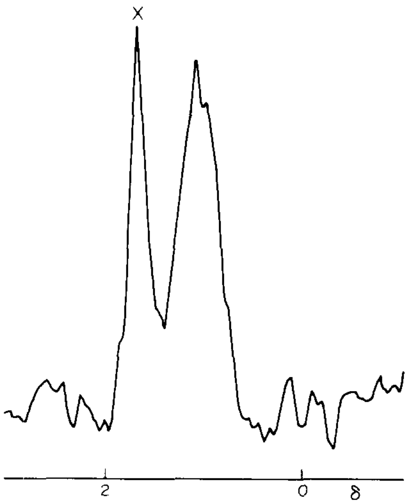

Fig. 3. Part of the ^{2}H-NMR spectrum of copolymer PEA-6. The peak marked X is due to occluded initiator; the fairly broad peak at ca 1.06δ is attributed to $(CD_3)_2C(CN)$-end-groups

initiator which could be eliminated by further purification of the polymer by reprecipitation. The corresponding peaks from the ^{2}H-end-groups in polyST and poly(methyl methacrylate) (PMMA) occurred at 1.02δ and 1.18δ respectively [6]. The chemical shift for CD_3- in the end-groups clearly depends on the identity of the attached monomeric unit; it might be possible therefore to determine the relative numbers of initiator fragments attached to the two types of monomeric unit in binary copolymers and then to compare the reactivities of the monomers towards the primary radical following the procedure already described for experiments involving [^{13}C]AIBN [1]. A copolymer of ST with MMA prepared with [^{2}H]AIBN gave rise however to a single unresolved resonance at a position intermediate between those for the homopolymers so that the comparison could not be made. A similar result was obtained for copolymers of ST with EA (PEA-5 and PEA-6); Fig. 3 shows a single unresolved peak at ca 1.06δ, between the positions for the $(CD_3)_2C(CN)$-group in the two homopolymers but close to that for the group in polyST. The effect resembles that found for copolymers of ST with MMA prepared with benzoyl-*carbonyl*[^{13}*C*] peroxide [3]; the benzoate end-groups in copolymers gave a single peak situated between those for the end-groups in the homopolymers. This result is somewhat surprising since Moad *et al.* [9] were able to distinguish between the end-groups $C_6H_5\cdot{}^{13}CO\cdot O\cdot CH_2\cdot CH(C_6H_5)$-, $C_6H_5\cdot{}^{13}CO\cdot O\cdot CH(C_6H_5)\cdot CH_2\cdot CH_2\cdot CH(C_6H_5)$- and $C_6H_5{}^{13}CO\cdot O\cdot CH(C_6H_5)\cdot CH_2\cdot CH(C_6H_5)\cdot CH_2$- in polyST; it must be noted however that these workers had the advantage of better resolution and greater sensitivity through the use of 62.9 MHz ^{13}C-NMR.

Copolymers of ST with EA were made using [^{13}C]AIBN. The ^{13}C-NMR spectrum of PEA-7 contained two equivalent peaks at 26.5–27.15δ and 27.85δ, corresponding to initiator fragments attached to ST units. For other copolymers, richer in EA (see Fig. 4), there was imbalance between the peaks attributed to ST-type end-groups; the areas under the two peaks were in the proportions 1:1.13 and 1:2.84 for PEA-8 and PEA-9 respectively. The differences between the areas can be explained if the upfield peak includes that for EA-type end-groups; on this basis

$$\frac{\text{no. of fragments attached to EA}}{\text{no. of fragments attached to ST}} = \frac{U - D}{2D} = n$$

where U and D are the areas under the upfield and downfield peaks respectively. The values of *n* for PEA-8 and PEA-9 are 0.07 and 0.92, respectively; the result for PEA-8 must be associated with a large relative error and the subsequent discussion is based on the result for PEA-9. The ratio of the two types

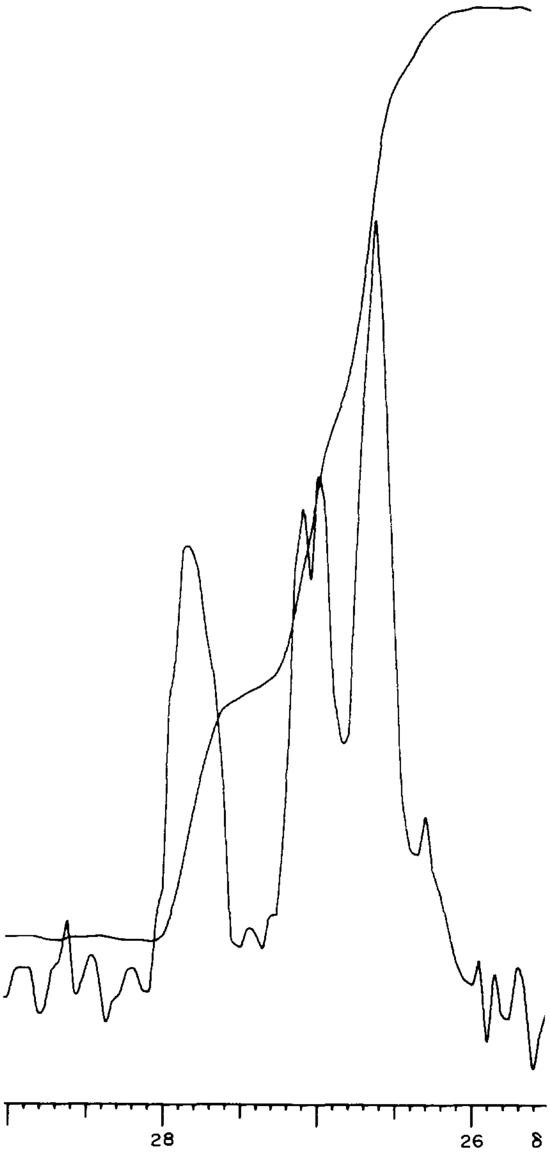

Fig. 4. Part of the ^{13}C-NMR spectrum of copolymer PEA-9. The peak at *ca* 27.8δ is attributed to $(^{13}CH_3)_2C(CN)$- groups attached to styrene; the peaks between ca 26.4 and 27.3δ are due in part to initiator fragments attached to styrene and in part to fragments attached to ethyl acrylate.

of end-group is related to the ratio of the concentrations of the monomers in the feed and to the velocity constants k′ and k″ for the reactions of the primary radical with EA and ST respectively, so that

$$\frac{\text{no. of } (^{13}\text{CH}_3)_2\text{C(CN)}\cdot\text{EA- groups}}{\text{no. of } (^{13}\text{CH}_3)_2\text{C(CN)}\cdot\text{ST- groups}} = n = \frac{k'[\text{EA}]}{k''[\text{ST}]}$$

It is deduced that k′/k″ is 0.3. Combination of this and previous results [1–3] shows that the relative reactivities of acenaphthylene, styrene, methyl methacrylate, methacrylonitrile, ethyl acrylate and vinyl chloride towards the 2-cyano-2-propyl radical at 60° are 4, 1.8, 1.0 (standard), 0.6, 0.6 and 0.07 respectively; the result for vinyl chloride refers to 45°. As for polymers of all other monomers so far examined [6], there is no evidence that AIBN gives rise to end-groups of more than one type in polyEA or that a radical $(\text{CH}_3)_2\text{C:C:N}\cdot$ is involved in initiation.

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