Polymer Bulletin 16, 209–214 (1986)

Polymer Bulletin

Comparisons of the reactivities of methacrylonitrile and acrylonitrile and of the corresponding polymer radicals

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Summary

It is confirmed that the polymethacrylonitrile radical is much less reactive than the polyacrylonitrile radical towards *trans*-stilbene. Methacrylonitrile and acrylonitrile are similar in their reactivities towards the 2-cyano-2-propyl radical and the benzoyloxy radical.

Introduction

This paper is concerned with aspects of the radical polymerizations of methacrylonitrile (MAN) and acrylonitrile (AN). The work began with consideration of the copolymerization of MAN (monomer-1) with *trans*-stilbene (STL); the monomer reactivity ratio, r_1, according to Lüssi (1) is 70 ± 40. This high value indicates that STL does not react readily with the polyMAN radical; it is line with the discovery (2) that STL is unreactive towards $(CH_3)_2C(CN)\cdot$ (to be regarded as a model for the polyMAN radical) although it reacts very readily with $C_6H_5.CO.O\cdot$. Lüssi (1) gave a value of 1.0 ± 0.1 for r_1 for the copolymerization of AN with STL. The large difference between the systems MAN/STL and AN/STL prompted a re-examination especially since Lüssi had determined the compositions of copolymers only by analyses for nitrogen. Copolymerizations have been performed using ^{14}C-labelled STL at low concentrations in the feeds; the high sensitivity of the tracer method allows accurate analyses of the copolymers and the derived values of r_1 seem to be reliable.

In a second stage of the work, the reactivities of MAN and AN towards primary radicals have been assessed by well documented methods. The reactivity of MAN towards $C_6H_5.CO.O\cdot$ was studied by the procedure involving benzoyl peroxide (BPO) labelled in the rings with tritium and at the carbonyl sites with carbon-14 (3). The reaction of AN with the 2-cyano-2-

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propyl radical was examined by the method making use of azobis(isobutyronitrile) (AIBN) enriched in its methyl groups with carbon-13 and of methyl methacrylate (MMA) as a reference monomer (4).

Experimental

All materials, either prepared or obtained commercially, were purified by standard procedures. Polymerizations were performed at 60°C under air-free conditions with dimethylformamide as diluent; conversions did not exceed 8%. Polymers were recovered by precipitation in methanol, purified by reprecipitation (three times for polymers prepared with radioactive initiator or comonomer) and dried in vacuum. Tests on the removal from unlabelled polymers of radioactive contaminants gave satisfactory results; the activities of polymers, as given in the results section, can therefore be properly attributed to chemically incorporated material.

^{13}C-NMR spectra were recorded, using a JEOL FX100 Fourier-transform spectrometer operating at 25.05 MHz, for solutions in d_6-dimethylsulphoxide; conditions were as specified previously (4). The specific activities of ^{14}C samples were determined using an LKB-Wallac "Spectral" 1219 Liquid Scintillation Counter. Samples of polymer were dissolved in dimethylformamide before being added to the toluene-butyl PBD scintillator solution. Corrections for quenching were made using the calibrated shift in the external standard spectrum for each sample.

Results and Discussion

Copolymerizations of MAN and AN with STL

Dilatometric studies showed that STL had very little effect upon the rate of polymerization of MAN with AIBN as initiator but caused some retardation for AN. Results of experiments involving ^{14}C-STL are shown in TABLE 1; monomer-1 is MAN or AN as appropriate.

TABLE 1

polymer	monomer-1	$[M_1]/[STL]$ in feed	disinteg min^{-1} g^{-1} for polymer
A	MAN	99.9	1.08×10^4
B	MAN	36.4	2.89×10^4
C	AN	126.3	7.87×10^5
D	AN	69.7	13.10×10^5

disinteg min^{-1} g^{-1} for ^{14}C-STL: 557×10^5

Copolymers MAN/STL and AN/STL can be represented as $(C_4H_5N)_n(C_{14}H_{12})_1$ and $(C_3H_3N)_m(C_{14}H_{12})_1$ respectively if the small contributions of end-groups are neglected. For scintillation counting in solution, (disinteg min^{-1} g^{-1} for STL)/(disinteg min^{-1} g^{-1} for MAN/STL copolymer) is (67n + 180)/180; the corresponding expression for AN/STL copolymer is (53m + 180)/180. AIBN was used as initiator for the copolymerizations so that STL was not incorporated preferentially at sites very close to end-groups (2). From data in TABLE 1, the values of n for polymers A and B are 13850 and 5180 and those of m for polymers C and D are 237 and 141.

STL (regarded as monomer-2) does not ordinarily undergo homopolymerization so that r_2 can be taken as zero for the systems MAN/STL and AN/STL. The copolymer composition equation is therefore used in the simplified form

$$(M_1/M_2)_{\text{copolymer}} = \frac{r_1[M_1]}{[M_2]} + 1$$

Values of r_1 from polymers A and B are 139 and 142; those from polymers C and D are 1.9 and 2.0. These values are about double those of Lüssi (1) but the large difference between MAN and AN in copolymerizations with STL is fully confirmed. The difference is made even more evident if the values of r_1 are used with those of k_p for the homopolymerizations to derive values of the velocity constants for the reactions between polyMAN and polyAN radicals and STL. For MAN at 60°C, k_p has been given as 201 (5) and 360 mol^{-1} l sec^{-1} (6); for AN, 1960 mol^{-1} l sec^{-1} has been quoted (7). Therefore the velocity constants for the reactions of polyMAN and polyAN radicals with STL are approx. 2 and 1000 mol^{-1} l sec^{-1} respectively.

Reactivities of MAN and AN towards primary radicals

The reactivities of many monomers towards the benzoyloxy radical have been compared (8) in terms of the velocity constants of the competing processes

$$\text{(i)} \quad C_6H_5.CO.O. \rightarrow C_6H_5. + CO_2 \qquad k_1$$

$$\text{(ii)} \quad C_6H_5.CO.O. + M \rightarrow C_6H_5.CO.O.M. \qquad k_2$$

The phenyl radicals formed in (i) subsequently enter polymer as end-groups. Taking k_1 as independent of the monomer, relative values of k_2 at 60°C for styrene (STY), vinyl acetate (VAC), MMA and AN are 1.00, 0.36, 0.12 and $\leqslant$ 0.05 respectively. The corresponding values found by an alternative method (9), allowing direct determination of the adduct formed in (ii), are 1.00, 0.26, 0.11 and 0.02. The only significant discrepancy occurs for VAC;

it may be accounted for, in part at least, by the occurrence in the polymerization of VAC of primary radical termination involving $C_6H_5.CO.O.$. This process would cause an underestimate of k_1/k_2 (and an overestimate of the reactivity of VAC) when using end-group analysis, since it would introduce an additional source of benzoate end-groups; it would not however affect the results obtained by the alternative method.

When using ^3H-^{14}C-BPO to initiate a homopolymerization (3)

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

$$\frac{^{3}\text{H disinteg rate for polymer}}{^{3}\text{H disinteg rate for BPO}} \times \frac{^{14}\text{C disinteg rate for BPO}}{^{14}\text{C disinteg rate for polymer}}$$

and this quantity is equal to $(k_2[M] + k_1)/k_2[M]$ where $[M]$ is the concentration of monomer during polymerization; k_1/k_2 can therefore be evaluated from the results of assays of polymer and peroxide (see TABLE 2). The value for polymer F may be unreliable because of the very low content of carbon-14; taking k_1/k_2 as 6.5 ± 1 mol l^{-1} gives the relative reactivity of MAN towards $C_6H_5.CO.O.$ as 0.06 (STY taken as unity). It is clear that MAN resembles AN in reactivity towards the $C_6H_5.CO.O.$ radical.

TABLE 2

polymer	[MAN] (mol l^{-1})	10^{-3}(disinteg min^{-1} g^{-1}) tritium	10^{-3}(disinteg min^{-1} g^{-1}) carbon-14	calc. k_1/k_2 (mol l^{-1})
E	7.96	96.4	2.87	6.33
F	2.56	31.7	0.45	7.40

10^{-6}(disinteg min^{-1} g^{-1}) for BPO; ^3H, 119.8; ^{14}C, 6.43

FIGURE 1 shows part of the ^{13}C-NMR difference spectrum for polyAN made using ^{13}C-AIBN and a polymer prepared similarly but with unenriched azonitrile. The prominent signals between 25 and 26.5δ are due to $(^{13}CH_3)_2C(CN)$- end-groups. FIGURE 1 also shows corresponding spectra for copolymers of AN with MMA. The signals at ca.29δ correspond to 50% of the initiator fragments attached to MMA units (i.e. R.MMA- groups); those at ca.26δ correspond to the remaining R.MMA- groups together with the R.AN- groups. Taking the areas under the peaks at ca.29δ and ca.26δ as P and Q respectively

$$\frac{\text{no. of R.AN- groups}}{\text{no. of R.MMA- groups}} = \frac{Q - P}{2P} = \frac{k_A[AN]}{k_M[MMA]}$$

where [AN] and [MMA] are the concentrations of monomers in the copolymerizing system and k_A and k_M are the velocity constants for the competing initiating

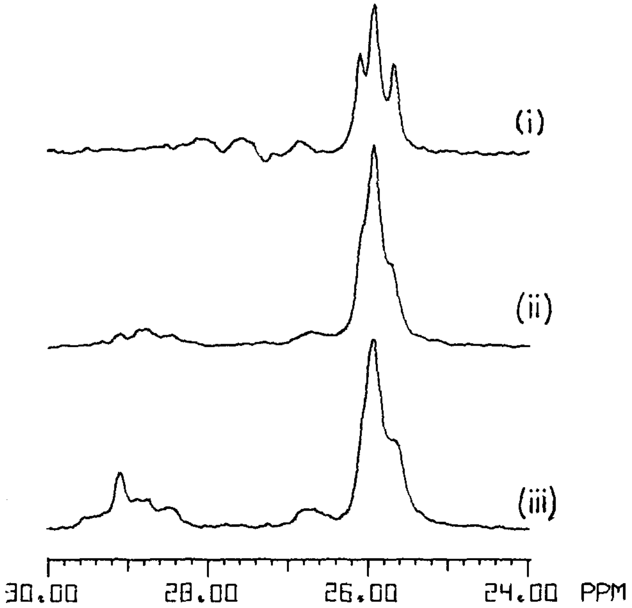

FIGURE 1. Parts of the ^{13}C-NMR spectra of polymers prepared using ^{13}C-AIBN. (i) homopolymer of AN; (ii) copolymer G; feed [AN] / [MMA] = 3.22; (iii) copolymer H; feed [AN] / [MMA] = 1.07.

processes. k_A/k_M is 0.79 for polymer G and 0.91 for polymer H; the former value is the less reliable because the signal at ca.29 δ is rather weak for polymer G so making evaluation of (Q - P)/2P rather uncertain. The relative reactivities of various monomers towards $(CH_3)_2C(CN)\cdot$ are:- STY, 1.00 (standard); MMA, 0.56; AN, 0.50; MAN, 0.34; VAC, 0.025. AN and MAN therefore do not differ greatly in reactivity towards the radical $(CH_3)_2C(CN)\cdot$.

General Conclusions

Bamford et al. (7) referred to the effect of methyl substitution at the alpha-carbon atom of a vinyl monomer, pointing out the resulting considerable reduction in k_p for homopolymerization; they suggested that radical reactivity, rather than monomer reactivity, is the dominating influence in the propagation reaction. This conclusion is supported by the similarity between AN and MAN in reactivity towards primary radicals; there is little chance of steric interference from the CH_3 group of MAN since attachment of the radical occurs at the CH_2 end of the double bond. This consideration does not apply however for the reactions of the polyAN and polyMAN radicals with monomers; for these reactions, the CH_3 group may have important effects. The lower reactivity of the polyMAN radical is particularly evident when considering reaction with STL, as pointed out by

Lüssi (1); the steric effect of the CH_3 group in the polymer radical is reinforced by the effect of the C_6H_5 groups in the unsaturated substance. At this stage, there seems to be no need to modify the previous conclusion (2) that steric considerations account for the large difference between the reactivities of $(CH_3)_2C(CN)$. and C_6H_5.CO.O. towards STL.

Further work is in progress for comparisons of the reactivities of (a) monomers CH_2:CHX and CH_2:C(CH_3)X towards radicals (b) the corresponding polymer radicals towards unsaturated substances particularly STL and (c) various primary radicals towards STL.

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Accepted August 4, 1986 C