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The Termination Mechanism for Radical Oligomerization of Methacrylonitrile

Algirdas K. Serelis and David H. Solomon

CSIRO, Division of Applied Organic Chemistry, G.P.O. Box 4331, Melbourne,
Victoria 3001, Australia

SUMMARY

Decomposition of azobisisobutyronitrile in benzene containing small amounts of methacrylonitrile produces a mixture of oligomers of methacrylonitrile. Analysis by gas chromatography-mass spectrometry indicates that combination is the preponderant (>90%) termination mechanism.

The termination reactions which occur in radical polymerization have been studied by a variety of methods, most of which rely on inferences based on bulk polymer properties or polymerization behaviour to elucidate the termination step (EASTMOND 1976), but none of which provide a direct chemical identification of the end products. Such approaches lack precision, and moreover, often produce erratic or even contradictory results. An alternative approach involves the use of small model systems which can lead to easily identifiable products and hence to a direct determination of the mechanism. The most notable successes of this approach have been with models for styrene polymerization, which largely confirm the accepted combination mechanism, but nevertheless reveal a significant degree of disproportionation (GIBIAN and CORLEY 1972; GLEIXNER et al. 1979; OVERBERGER and FINESTONE 1955). Model chemistry of polymers is subject to criticism, however, in that the size difference between the polymer radical and the relevant model radical could have a significant effect on chemical behaviour. We have attempted to counter this objection by examining model systems which are in fact propagating radicals, but which are still of small enough size that their termination products are manipulable and characterizable by standard techniques. Our approach is exemplified by the study of termination in methacrylonitrile (MAN) polymerization as described herein.

BAMFORD et al. (1969) studied the termination of MAN polymerization by a gelation technique and concluded that it involved 35% combination. This result, however, stands in contrast with the self-reactions of 2-cyanoprop-2-yl radicals (CPR) (BICKEL and WATERS 1950b; HAMMOND et al. 1955, 1960) and related species (DOX 1925) which are known to involve >90% combination. We have sought to clarify this apparent contradiction by studying more polymer-like radicals formed by generating CPR from azobisisobutyronitrile (AIBN) in the presence of small amounts of added MAN. Under these

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conditions, propagation is limited to only a few steps and the oligomers thus produced can be analyzed by standard methods. Quantitative analyses were done by gas-liquid chromatography. MAN and isobutyronitrile (IBN) were identified by comparison with authentic samples on g.l.c. Tetramethylsuccinonitrile (TMSN) and trinitrile (3) were isolated by crystallization and column chromatography respectively and characterized spectroscopically. The structures of the remaining products were deduced from their mass spectra, g.l.c. behaviour, and a consideration of relative yields (Table 1). Efforts directed toward more complete characterization are currently in progress.

TABLE 1

Products of decomposition of AIBN (0.10 M) in the presence of MAN in benzene at 80°

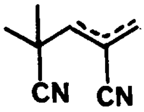
[MAN] added	-^{B}	0.10 M	0.20 M
Product		% Yield^{A}	
MAN	0.96	13.9	30.6
IBN	7.4 (7.5)	3.3 (3.8)	2.0 (2.9)
TMSN	83.1 (83.9)	25.5 (29.6)	14.7 (21.2)
(1)	0.27 (0.27)	2.3 (2.7)	2.4 (3.5)
(2)	0.30 (0.30)	2.8 (3.3)	2.6 (3.7)
(3)	7.0 (7.1)	26.8 (31.1)	16.2 (23.3)
(4)+(5)	-	1.4 (1.7)	2.6 (3.8)
(6)	0.61 (0.62)	12.8 (14.9)	13.4 (19.3)
(7)	0.37 (0.37)	6.4 (7.4)	6.2 (8.9)
(8)	-	0.06 (0.07)	0.38 (0.55)
(9)	-	0.07 (0.08)	0.45 (0.65)
(10)	-	2.8 (3.3)	5.1 (7.3)
other^{C}	-	1.3 (1.5)	2.4 (3.5)
other^{C}	-	0.49 (0.57)	0.84 (1.2)

[A] Numbers in parentheses are yields normalized to exclude MAN.

[B] No MAN added. MAN generated in situ by disproportionation of CPR.

[C] Isomeric with (10)

The currently available information is insufficient to define the position and stereochemistry (if applicable) of the double bond in the unsaturated products (1), (4) and (8). It is noteworthy, however, that under all conditions on a variety of columns only one peak could be seen for each product, implying a high degree of selectivity for the hydrogen abstraction process. Significantly, the similarities in yields of the saturated and unsaturated partners in each pair of disproportionation products suggests little or no preference for either abstraction or donation by either of the radicals of a disproportionating pair. It should be noted, however, that other systems have been reported in which the hydrogen transfer in disproportionation appears to be mainly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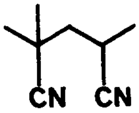
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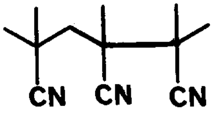
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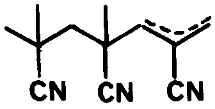
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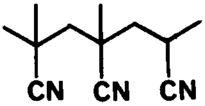
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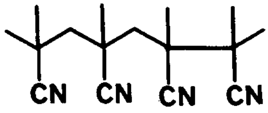
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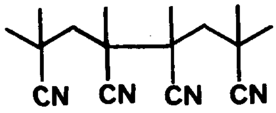
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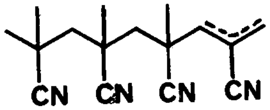
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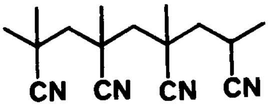
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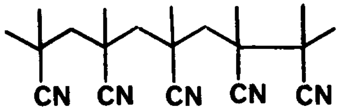
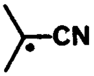
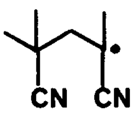

(10)

from the smaller to the larger radical (BICKEL and WATERS 1950a; TRECKER and FOOTE 1968).

Termination of the propagating radicals occurs mainly by reaction with CPR (primary radical termination), although at higher MAN concentrations the extent of termination not involving CPR increases. It is therefore significant from the standpoint of CPR being a valid model for polymethacrylonitrile radical that the overall ratio of combination to disproportionation (c/d)* remains nearly constant over all three experiments, viz., c/d = 11.8, 11.5, and 9.6 for [MAN]=0, 0.10 and 0.20 M respectively. This change in c/d, which corresponds to a decrease in combination from 92.2% to 90.5% with increasing [MAN], can be explained by the increasing intrusion of disproportionation products corresponding to undetected higher molecular weight combination products.


CPR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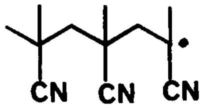
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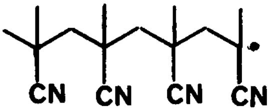
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* For comparison purposes, yields of disproportionation products are taken as the average of the saturated and unsaturated pairs, except in the case of IBN, where MAN cannot be accounted for due to its consumption by propagation.

Individual comparisons are complicated by the uncertainty in the source of disproportionation products. Thus, if the reaction of CPR with radical (11) is taken as the sole source of (1) and (2), then c/d=10.7 and 6.4 (for [MAN]=0.10 M and 0.20 M). However, (1) and (2) can also arise by the self-reaction of radical (11), or by reactions between (11) and (12), (11) and (13), etc. If the yields of (1) and (2) are apportioned between the processes CPR+(11) and (11)+(11) according to the yields of the corresponding combination products (3) and (7), then c/d=13.2 at 0.10 M MAN and 8.9 at 0.20 M MAN. This drift again highlights the effect of contributions from disproportionation of (11) with higher radicals (eg. (12), (13), etc.) becoming more important at higher MAN concentrations. However, since these contributions decrease toward lower [MAN], we can safely regard c/d ≈ 13 as a lower limit for the reactions CPR+(11) and (11)+(11).

The production of (4) and (5) occurs mainly by disproportionation of CPR with (12) in competition with their combination to form (6). On this basis, c/d=17.6 and 10.3 at 0.10 and 0.20 M MAN. A correction for the alternative reactions (11)+(12), (12)+(12) etc. which also lead to (4) and (5) cannot be made in this case because of uncertainties in the identification of the corresponding combination products. These, however, would again have the effect of lowering the above value of c/d, so that c/d ≈ 18 can be taken as the lower limit for the reaction CPR+(12). Similarly, comparison of disproportionation products (8) and (9) with combination products (10) at [MAN]=0.20 M indicates a minimum value of c/d ≈ 12 for the reaction CPR+(13).

Some general comments are pertinent at this point. GIBIAN and CORLEY (1973), have collated a large body of data on radical-radical reactions. From the examples cited, it appears that c/d shows no marked sensitivity toward structural variations beyond the immediate vicinity of the radical centre. Furthermore, regardless of the presence of a large number of β-hydrogens at the radical centre, which does in general favour disproportionation, strongly delocalized radicals, such as those bearing α-phenyl and α-cyano substituents undergo predominant combination. Finally, although combination is usually increased at higher temperatures, the observed changes in c/d are usually very small.

Thus, while we acknowledge the uncertainties inherent in extrapolating from small radical systems to macroradicals, we nevertheless believe that our results present a strong case for the predominance of combination termination in the polymerization of methacrylonitrile. A detailed account of our work containing an analysis of relevant earlier results will be reported elsewhere.

EXPERIMENTAL

Benzene was recrystallized three times, dried by azeotropic distillation of water, and distilled. MAN was carefully fractionated through a 30cm vacuum-jacketed Vigreux column immediately before use. AIBN was recrystallized twice from methanol (m.p. 101-3°). Benzene solutions containing 0.10 M AIBN and 0, 0.10 and 0.20 M MAN were degassed by several liquid N_2 freeze-evacuation-thaw cycles, sealed under vacuum, and heated at 80° for 24 hr. Gas chromatography was carried out on a Varian Vista 4600 fitted with a flame ionization detector and attached to a Varian Vista CDS 401 data system. For the determination of volatile components, the column used was FFAP, SCOT, 5.2mx0.5mm; 4.0 ml/min He; 50° for 10 min, then 50-220° at 20°/min. Oligomer analysis was on a column of 5% Dexil 410 on 100/120 Chromosorb W(HP), glass, 2.0mx2.0mm; 25 ml/min He; 70°-300° at 7°/min. G.l.c.-mass spectral determinations were done on a 5% Dexil 410 column in a Finnigan 3300 mass spectrometer using methane as a reagent/carrier gas.

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