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STUDY OF CYANO-DERIVATIVES OF PROPENE AS TRANSFER AGENTS IN RADICAL POLYMERIZATIONS

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ABSTRACT

A new procedure for determining transfer constants, depending on knowledge of the numbers of initiator fragments in the average molecules of appropriate polymers, has been applied to crotononitrile (1-cyano-1-propene) and allyl cyanide (3-cyano-1-propene) with methyl methacrylate and styrene at 60°C. Allyl cyanide is the more reactive of the two additives, but is less effective than allylbenzene (3-phenyl-1-propene); neither of the cyano-derivatives causes appreciable retardation.

INTRODUCTION

An account has been given [1] of a procedure for finding a transfer constant by consideration of the number ($\underline{n}$) of initiator fragments in the average molecule of a polymer prepared under controlled conditions in the presence of a transfer agent. The method can be extended [2] to transfer agents which cause retardation of the polymerization i.e. to cases of degradative transfer. The substances already examined include 3-phenyl-1-propene (allylbenzene) (AB) and the E-isomer of 1-phenyl-1-propene (β-methylstyrene) (BMS) [3] which might give rise to the radicals $CH_2{:}CH{\cdot}CH{\cdot}Ph$ and ${\cdot}CH_2{\cdot}CH{:}CH{\cdot}Ph$, respectively. These radicals can be regarded as equivalent because of delocalization; it causes them to be stabilized and inefficient in re-initiation so that the parent substances are expected to be degradative transfer agents.

It was confirmed that AB, at quite low concentrations, causes quite pronounced retardation of the polymerizations at 60°C of methyl methacrylate (MMA) and styrene (STY) initiated by azobisisobutyronitrile(AIBN). End-group analyses showed that the values of n for polymers prepared in the presence of AB are appreciably less than those for polymers made under similar conditions, but without the additive being present. It was deduced that, when allowance is made for retardation,the transfer constants for AB/MMA and AB/STY are both in the region of 5×10^{-3}. There was no reason to doubt that AB acts as a conventional transfer agent by giving up a hydrogen atom to yield a comparatively unreactive radical. BMS was found to be an effective retarder but end-group analysis revealed that the presence of BMS during the polymerization of MMA caused n for the resulting polymer to be significantly greater than for a case in which the additive was absent. Evidently, AB and BMS act in very different ways. The results were consistent with the view that BMS occasionally adds to a growing radical, that the product is deactivated by reaction with another radical and that this process of termination occurs, in part at least, by combination according to Scheme 1.

$$\begin{aligned} P_n\cdot + \mathrm{BMS} &\rightarrow P_n\cdot\mathrm{BMS}\cdot \\ P_n\cdot\mathrm{BMS}\cdot + P_m\cdot &\rightarrow P_n\cdot\mathrm{BMS}\cdot P_m \end{aligned} \qquad (1)$$

There is a formal resemblance to the action of p.benzoquinone as a retarder for the polymerization of MMA [4]; in that case, the incorporation of the expected quantity of the quinone in the polymer was confirmed by the results of experiments involving ^{14}C-benzoquinone. The inclusion of BMS in the polymer was not established directly, the quantity being insufficient for reliable detection by NMR techniques and the use of ^{14}C-labeled material being impracticable; support for the suggested scheme, however, was provided by consideration of the values of $\overline{M}_w/\overline{M}_n$ for the polymers [5]. It is possible that BMS functions in two ways, viz. partly according to Scheme 1 and also to some extent as a conventional transfer agent.

It is unlikely that the special behavior of BMS could have been established except by the study of the end-groups derived from the initiator. It was decided to check whether or not Scheme 1 might be applicable to other derivatives of propene. The substances examined were crotononitrile (1-cyano-1-propene) (CRN) and allyl cyanide (3-cyano-1-propene) (ALC); they would be expected to give rise to the equivalent radicals $\cdot CH_2\cdot CH:CH\cdot CN$ and $CH_2:CH\cdot CH\cdot CN$.

Bartlett *et al.* [6] studied transfer to monomer for allyl acetate. Zubov *et al.* [7] examined various allylic compounds $CH_2:CH\cdot CH_2X$; they related the polymerizability in radical systems and the importance of degradative transfer to the nature of the substituent X and its effect upon the strength of the C-H bonds in the group $-CH_2X$. More recently, there has been considerable interest in the behavior of rather more complex allylic compounds during radical polymerizations [8] but there has been comparatively little study of fundamental aspects of the reactions in polymerizing systems of simpler compounds such as ALC.

There is a scarcity of published information [9] on copolymerizations of compounds such as ALC and CRN with MMA and STY, but it is clear that normally the incorporation of the allylic compound is only slight. If, however, it occurred to an appreciable extent, the solution properties of the products might differ significantly from those of the homopolymers of MMA and STY so that false results might be obtained by Size Exclusion Chromatography (SEC) involving the use of standard homopolymers as calibrants; this effect would mean that determinations of $\underline{n}$ might be seriously impaired. Further, calculations of kinetic chain lengths (ν) would be affected if the compositions of the actual polymers were appreciably different from those corresponding to homopolymers of the principal monomers. Systematic studies of copolymerizations involving ALC and CRN have not been undertaken but some experiments have been performed to obtain information on the extents to which the additives become combined in polySTY.

EXPERIMENTAL

The monomers and initiator were purified by standard procedures; the azonitrile was labelled in its nitrile groups with carbon-14. The two unsaturated additives were redistilled. ^1H-NMR revealed that the sample of CRN contained the E- and Z-isomers in the ratio 1:3.1 and that the proportions were hardly changed by repeated distillation (see Appendix).

Polymerizations were performed at 60°C under anaerobic conditions in dilatometers using benzene as diluent; in each case, the total volume of the reacting system was close to 4 ml. It was assumed that conversion factors were unaffected by the presence of the additives. There were no inhibition periods for the polymerizations and plots of contraction vs. time were linear; consumption of monomer did not exceed 7%.

Polymers were recovered by precipitation in methanol, purified by three reprecipitations and finally dried in vacuum at room temperature to constant weight. Activities of polymers and initiator were measured by scintillation counting of solutions. Molecular weights of polymers were found by SEC using standard polymers as calibrants [3] and supposing that any incorporation of the additive in the polymers caused negligible effects. With the same assumption, values of ν in the polymerizations were given by $82a_i/Ma_p$ where a_i and a_p are the activities in Bq g^{-1} of initiator and polymer respectively, and M is the formula weight of the principal monomeric unit (MMA or STY). The rate of initiation (R_i) was found as R_p/ν, where R_p is the rate of polymerization, and $\underline{n}$ as $\overline{DP}_n/\nu$ [10].

^{1}H-NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL GSX-400 spectrometer.

RESULTS AND DISCUSSION

The amounts of ALC and CRN incorporated in polymers were judged from examination of ^{1}H-NMR spectra of appropriate samples of polySTY. The spectral areas corresponding to aromatic and aliphatic hydrogens (A_{ar} and A_{al}, respectively) were compared for polymers prepared from systems similar to those used in the main experiments. The composition of a polymer prepared using STY with either ALC or CRN can be represented as $(C_8H_8)_1(C_4H_5N)_a$ since its molecular weight is sufficient for initiator fragments to make only negligible contributions. For the ^{1}H-NMR spectra

$$\frac{A_{ar}}{A_{al}} = r = \frac{5}{3+5a}$$

so that, knowing r, a can be calculated. Results in Table 1 show that incorporations of the additives are only slight; $\overline{DP}_n$ for both polymers is of the order of 120 so that molecules contain on average approximately four units derived from the additive. It is unlikely that incorporation at this level has significant influence on determination of $\overline{M}_n$ by SEC or of ν by end-group analysis. Similar conclusions are most probably applicable to the samples of polyMMA.

TABLE 1. ^{1}H-NMR Spectra of Samples of Polystyrene

[additive]/[STY] during polymerization	A_{ar}/A_{al} for polymer (r)	[additive]/[STY] in polymer (a)
ALC; 0·72	1·59	0·029
CRN; 0·42	1·57	0·037

Table 2 refers to polymerizations involving ^{14}C-AIBN and ALC or CRN and also to the resulting polymers. The additives at concentrations up to about 4 mol dm^{-3} hardly affected R_p; in contrast, AB at about 0.25 mol dm^{-3} caused R_p for MMA to fall by a factor approaching two [3]. The derived values of R_i/[AIBN] are close to those expected for polymerizations at 60°C, indicating that ALC and CRN do not appreciably affect the rate of incorporation of initiator fragments; their effects on $\underline{n}$ for the resulting polymers are therefore not attributable to interference with the process of initiation. The values of R_i/[AIBN] for polymerizations of MMA are a little below those for STY; the difference can be explained in terms of losses of some of the smaller molecules of polyMMA during precipitation in methanol [5].

The values of $\underline{n}$ expected for polyMMA and polySTY, prepared at 60°C in the absence of transfer processes, are 1.05 and 1.60, respectively in quite good agreement with the results for polymerizations numbers 5 and 10; it appears that $\underline{f}$ (the fraction of terminations occurring by combination) is 0.10 for MMA and 0.75 for STY [3]. The expression has been used to calculate transfer constants. As explained previously [3], allowance properly should be made for transfers to benzene and monomer but neglect of these processes leads only to small over-estimates of the transfer constants. Modifications to allow for degradative transfer, necessary for the phenyl derivatives of propene, are not required for ALC and CRN.

$$\frac{k_f}{k_p} = \frac{[\text{monomer}]}{[\text{transfer agent}]} \times \frac{2 - 2\underline{n} + \underline{n}\underline{f}}{2\underline{n}}$$

The derived transfer constants are very sensitive to quite small changes in $\underline{n}$. To illustrate that point, the last column of Table 2 shows in each case two values of k_f/k_p, the first based upon ($\underline{n}$ -0.04) and the other upon ($\underline{n}$ + 0.04). Experience has

TABLE 2. Polymerizations Involving Crononitrile or Allyl Acyanide

no.	monomer	[additive]	10^2[AIBN]	10^5R_p	$\overline{M}_n$	polymer activity	ν	10^5R_i/[AIBN]	n	$10^4k_f/k_p$
1	MMA	CRN; 2·80	0·98	7·19	64800	1530	701	1·03	0·92	2·05; 1·03
2	MMA	CRN; 1·96	0·98	7·19	68900	1530	701	1·03	0·98	1·75; 0·46
3	MMA	ALC; 2·83	1·11	7·58	49100	1543	695	0·98	0·71	5·96; 4·19
4	MMA	ALC; 1·41	1·04	7·58	55700	1535	699	1·03	0·80	7·96; 5·25
5	MMA	–	1·05	7·49	72000	1530	701	1·02	1·03	–
6	STY	CRN; 4·10	2·87	4·18	20500	7880	131	1·11	1·50	4·64; 1·89
7	STY	CRN; 2·34	3·03	4·37	19900	8170	126	1·15	1·52	7·15; 2·26
8	STY	ALC; 3·56	3·45	4·83	13500	8217	125	1·11	1·04	35·5; 28·1
9	STY	ALC; 2·37	3·16	4·54	16700	8117	127	1·13	1·27	26·0; 19·1
10	STY	–	2·90	4·85	24500	6870	150	1·12	1·57	–

For MA, [monomer] = 2·15 mol dm^{-3}; for STY, [monomer] = 4·16 mol dm^{-3} additive and [AIBN] in mol dm^{-3}

Rp in mol dm^{-3} s^{-1}

Polymer activity in Bq g^{-1}; activity of AIBN = 13·08 x 10^5 Bq g^{-1}

$R_{i/}$[AIBN] in s^{-1}

shown that it is unrealistic to expect uncertainties of less than ± 0.04 in experimentally determined values of n for systems of the types under consideration; for polymers numbers 4 and 9, the variations in n would correspond to changes in M_n of only ± 2800 and ± 600, respectively.

The selected values of k_f/k_p are :
for CRN with MMA and STY, 1.4×10^{-4} and 3.5×10^{-4} respectively
for ALC with MMA and STY, 5.6×10^{-4} and 2.7×10^{-4} respectively.

It appears that ALC is more reactive than CRN as a transfer agent in the polymerizations of the monomers and that both are considerably less reactive than AB.

It is necessary to note that the two isomers of CRN might differ appreciably in reactivity. The ratio of E-isomer to Z-isomer was 1:3.1 and so, for the extreme case of the former being entirely responsible for the reactivity, the quoted transfer constants:f-or CRN should be increased by a factor of 4.1; on the other hand, if the E- isomer is completely unreactive, the values of k_f/k_p applicable to the Z-isomer should be increased by a factor of 1.3. Walling [11] discussed the differences between the E- and Z-isomers of certain unsaturated compounds in radical-addition processes; it has also been shown [12] that the E-isomers of stilbene and some related compounds are much more effective than the Z-isomers in capturing the benzoyloxy radical. It is reasonable to suppose that any difference between the reactivities as transfer agents of the E- and Z-isomers of a particular compound is rather less than in radical-additions since the double bond is not directly involved in the hydrogen- abstraction.

The study now reported gives no indication that either ALC or CRN behaves unexpectedly when used as an additive during the radical polymerization of STY or MMA at 60°C. It appears that they undergo limited copolymerization and that they function as transfer agents of moderate reactivity by the process of hydrogen-abstraction; the resulting radicals reinitiate quite efficiently so that ALC and CRN do not act as degradative transfer agents.

When considering AB as a transfer agent, attention was paid also to 2-phenylpropene (α-methylstyrene) (AMS). A suitable direct study of AMS could not be made because it engages quite readily in copolymerizations although the ceiling temperatures for its homopolymerizations are low. It was pointed out [3] that there is no evidence either that transfer to monomer is particularly important for AMS or that the process, when it occurs, is degradative; in these respects, AMS differs from AB. It might be interesting also to compare transfer to 2-cyanopropene (methacrylonitrile) (MAN) with transfers to the other cyano-derivatives of propene

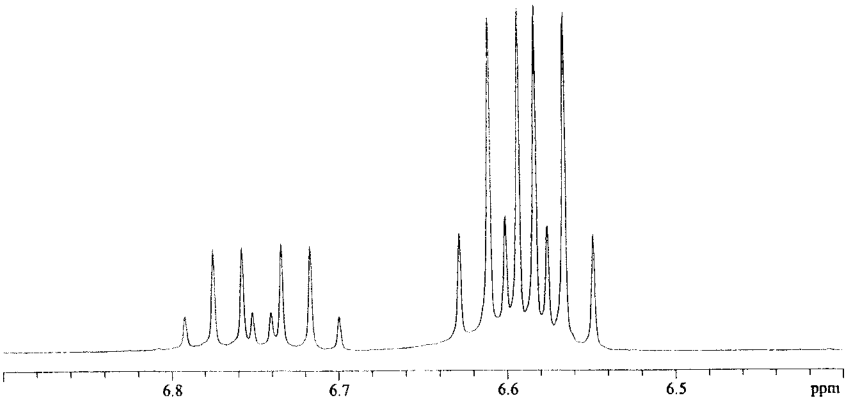

Figure 1. 400 MHz ^{1}H-NMR Spectrum of Crononitrile.

i.e. ALC and CRN. The ready polymerization of MAN means that, as in the case of AMS, it is necessary to consider the value of k_m/k_p for transfer to monomer in it own polymerization. It appears that the process for MAN occurs comparatively readily; k_m/k_p has been given [13] as 5.8 x 10.4 at 60°C (i.e. generally similar to the transfer constants now found for ALC and CRN during polymerizations of MMA and STY), whereas values of k_m/k_p for many other monomers are less than 10^{-4} [14].

APPENDIX

The ^{1}H-NMR spectrum for the sample of crotononitrile contains two multiplet signals at 6.59 and 6.74 ppm (see Figure 1); for both components of the sample, they arise from an olefinic proton. The signals have intensities in the ratio 3.1:1. The larger response must arise from the isomer in which the geometry of substitution is *cis*; a spin-spin couplingof ca. 11 Hz is present as a doublet. The smaller multiplet contains a doublet with coupling of ca.16 Hz; this larger olefinic coupling is typical for the *trans* isomer.

REFERENCES

[1] C. A. Barson, J. C. Bevington, and B. J. Hunt, *J. Polym. Sci., Part A. Polym. Chem., 33*, 863 (1995).

[2] C. A. Barson, J. C. Bevington, and B. J. Hunt, *Ibid., 34*, 227 (1996).

[3] C. A. Barson, J. C. Bevington, and B. J.Hunt, *Polymer,* in press.

[4] J. C. Bevington, N. A. Ghanem, and H. W. Melville, *Trans. Faraday Soc., 51*, 946 (1955).

[5] C. A. Barson, J. C. Bevington, and B. J. Hunt, *Eur. Polym. J.*, in press.

[6] P. D. Bartlett and R. Altschul, *J. Am. Chem. Soc., 67*, 810 (1945).

[7] V. P. Zubov, M. V. Kumar, M. N. Masterova, and V. A. Kabanov, *J. Macromol. Sci., Chem., A13*, 111 (1979).

[8] G. Moad and D. H. Solomon, *The Chemistry of Free Radical Polymerization*, Pergamon, Oxford, 1995, p. 246.

[9] R. Z. Greenley, in *Polymer Handbook*, 3rd. Ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1989, p. II, 171.

[10] J. C. Bevington, B. J. Hunt, and C. A. Barson, *Macromol. Symp., 111*, 293 (1996).

[11] C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, p. 128.

[12] J. C. Bevington, *Angew. Makromol. Chem., 185/186,* 1 (1991).

[13] N. Grassie and E. Vance, *Trans. Faraday Soc., 52*, 727 (1956).

[14] F. Hraba'k, J. Lokaj, J. Bila, K. Bouchal, and J. Stokr, *Makromol. Chem., Rapid Commun., 3*, 89 (1982).

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