Reactivities of methyl vinyl ketone and methyl isopropenyl ketone towards the 1-cyano-1-methylethyl radical: general consideration of steric effects in the reactions of monomers with polymer radicals

K. Behari*, J. C. Bevington† and T. N. Huckerby

Department of Chemistry, The University, Lancaster LA1 4YA, UK
(Received 7 January 1988; revised 17 March 1988; accepted 22 March 1988)

[13]C nuclear magnetic resonance has been used to study the end-groups, derived from azobis(isobutyronitrile), in homopolymers of methyl vinyl ketone (MVK) and methyl isopropenyl ketone (MIPK) and in binary copolymers of those monomers with methyl methacrylate (MMA). Both MVK and MIPK are more reactive than MMA towards the 1-cyano-1-methylethyl radical, by factors of 2.4 and 1.4, respectively. There is general discussion of the effects on reactivity of introducing an α-methyl group into a monomer. For the cases considered, the substitution has some influence on the reactivities of the monomers but it reduces markedly the reactivities of the derived polymer radicals in their reactions with various monomers; the effects on the polymer radicals may be caused by steric interference due to the methyl group.

(Keywords: methyl vinyl ketone; methyl isopropenyl ketone; methyl methacrylate; copolymerization; end-groups; steric effects)

INTRODUCTION

The polymerization of vinyl ketones was reviewed in 1959[1] and 1972[2]. These monomers still attract attention largely because of interest in the photochemistry and photophysics of their polymers and copolymers. During work on radical copolymerizations involving methyl vinyl ketone (MVK) and methyl isopropenyl ketone (MIPK), the opportunity arose to examine the nature of the end-groups in polymers prepared using azobis (isobutyronitrile) (AIBN) as initiator. It was then possible to compare these ketonic monomers with other monomers in their reactivities towards the 1-cyano-1-methylethyl radical derived from AIBN. Some polymers containing carbonyl groups are not made directly from the appropriate ketonic monomers; thus poly(α-methyl vinylacetophenone) has been prepared by acetylation of poly(α-methylstyrene)[3]. In such cases, the pattern of end-groups for the derived polymer is governed by that for the parent polymer unless the end-groups also are modified by the chemical treatment.

In the work described in this Paper, use was made of the azonitrile enriched with carbon 13 in its methyl groups (^{13}C-AIBN) followed by study of the end-groups by ^{13}C nuclear magnetic resonance (n.m.r.) The chemical shifts for the n.m.r. signals arising from a $(CH_3)_2C(CN)$– end-group are affected significantly by the nature of the monomeric unit attached to it[4]. Generally, for a copolymer of monomers M_1 and M_2, prepared using ^{13}C-AIBN, the end-groups $(CH_3)_2C(CN).M_1$– and $(CH_3)_2C(CN).M_2$– give n.m.r. signals which can be distinguished. The numbers of the two types of end-group can be compared by integration of the spectrum; then, knowing $[M_1]/[M_2]$ in the feed, it is possible to evaluate k_1/k_2, where k_1 and k_2 are the velocity constants for the addition of $(CH_3)_2C(CN)$. to M_1 and M_2, respectively. In the present work, homopolymers of MVK and MIPK were first prepared using ^{13}C-AIBN. The monomers were then separately copolymerized with methyl methacrylate (MMA) using the enriched initiator; MMA was thus used as the reference monomer for comparisons of reactivities.

EXPERIMENTAL

Monomeric MMA was purified by standard procedures. MVK (Fluka) and MIPK (Wolff & Kaaber, Farum, Denmark) were repeatedly fractionated at reduced pressure in N_2. The preparation of ^{13}C-AIBN has been described elsewhere[5]. Polymerizations and copolymerizations were performed at 60°C in dilatometers under air-free conditions with dimethylformamide as diluent; in each case, the total concentration of monomers was $\approx 6 \, mol \, dm^{-3}$ and that of initiator $\approx 1.5 \times 10^{-2} \, mol \, dm^{-3}$. Conversions were restricted to 10%; there were no kinetic abnormalities. Polymers and copolymers were recovered by precipitation in methanol, purified by reprecipitation and finally dried in vacuum. [13]C n.m.r. spectra were recorded using a JEOL FX100

*On study leave from Department of Chemistry, University of Allahabad, Allahabad, India
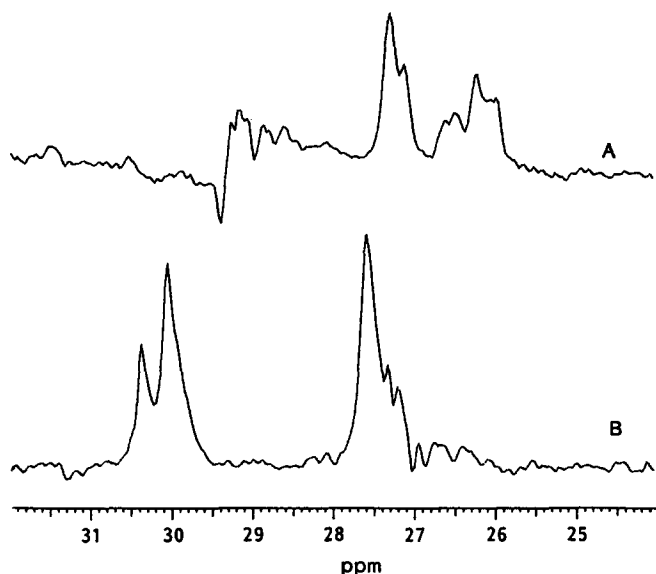†To whom correspondence should be addressed

Figure 1 ^{13}C n.m.r. spectra for homopolymers of methyl vinyl ketone (spectrum A) and methyl isopropenyl ketone (B), prepared at 60°C using ^{13}C-AIBN

Fourier transform spectrometer operating at 25.05 MHz; the conditions have been specified elsewhere[5]. It was necessary to use difference spectra to eliminate interference between the end-group signals and those arising from carbon atoms in the monomeric units; from the spectrum for a polymer or copolymer prepared using ^{13}C-AIBN was subtracted the spectrum for a material prepared similarly but with unenriched AIBN.

RESULTS AND DISCUSSION

Figure 1 refers to homopolymers of MVK and MIPK; it shows those parts of the 25 MHz ^{13}C n.m.r. difference spectra which include signals arising from the methyl groups in the initiator fragments which form end-groups. In both cases, the methyl groups give rise to two separate resonances covering equal areas in the spectra, because the monomeric units possess chiral sites. For polyMVK, the signals occur between $\delta = 25$ and 28 ppm; for polyMIPK, they are found at $\delta \approx 27.5$ and 30 ppm. The spectra in *Figure 1* give no sure indication that AIBN gives rise to significant numbers of groupings other than $(CH_3)_2C(CN).CH_2.CX(COCH_3)$– where X is H or CH_3, resulting from tail-addition of $(CH_3)_2C(CN).$ to monomer.

The polymers of MVK rapidly discoloured in $CDCl_3$, used as the n.m.r. solvent. The structural changes responsible for this effect may have occurred to slightly different extents for the two polymers used for the construction of a difference spectrum, so accounting for the rather poor quality of spectrum A.

The end-group signals possess fine structure which must be associated with stereochemical relationships between the monomeric units close to the initiator fragments. The separation of the peaks is much less for polyMVK than for polyMIPK. This effect seems to be quite general for $(CH_3)_2C(CN)$– end-groups attached to units $-CH_2.CHX$– and $-CH_2.C(CH_3)X$–, the presence of the α-methyl group causing greater separation of the peaks also when X is $COOCH_3$, C_6H_5 and CN.

Figure 2 contains parts of the difference spectra for copolymers of MIPK with MMA, prepared using ^{13}C-

AIBN. In each case, the total area covered by the overlapping downfield signals near $\delta = 30$ ppm is equal to the total area covered by the upfield signals between $\delta = 25$ and 28 ppm. The peak at $\delta \approx 27.5$ ppm grows at the expense of that at $\delta \approx 25.5$ ppm, with increase in the value of [MIPK]/[MMA] in the feed. The 25.5 and 27.5 ppm peaks are therefore associated with $(CH_3)_2C(CN).MMA$– and $(CH_3)_2C(CN).MIPK$–, respectively; these end-groups are referred to as R.MMA– and R.MIPK–, respectively. For systems in which [MIPK]/[MMA] in the feed had values of 0.36, 1.09 and 3.23, the values of (area for R.MIPK-end-groups)/(area for R.MMA– end-groups) are 0.53 ± 0.20, 1.45 ± 0.15 and 4.55 ± 0.12, respectively. Application of the relationship

$$\frac{\text{no. of R.MIPK– end-groups}}{\text{no. of R.MMA– end-groups}} = \frac{k_{\text{MIPK}}[\text{MIPK}]}{k_{\text{MMA}}[\text{MMA}]}$$

where the velocity constants refer to the reactions of the monomers with the $(CH_3)_2C(CN).$ radical, leads to values of 1.47 ± 0.55, 1.35 ± 0.14 and 1.41 ± 0.04 for $k_{\text{MIVK}}/k_{\text{MMA}}$, with an average of 1.4; the uncertainties arise from imperfect separation of peaks in the spectra and probably also in part from slight mismatch between the copolymers used to construct a difference spectrum. The negative peak at $\delta \approx 25$ ppm in spectrum A can be explained by incomplete purification of the copolymer prepared with unenriched AIBN, leading to retention of a small amount of initiator.

Parts of the difference spectra for copolymers of MVK with MMA, prepared using ^{13}C-AIBN, are shown in *Figure 3*. The rather low concentrations of the enriched end-groups and the uncertainties already mentioned led to difference spectra of rather poor quality. The downfield resonance at $\delta \approx 30.2$ ppm, associated with R.MMA– end-groups, is, however, isolated and so it is possible to
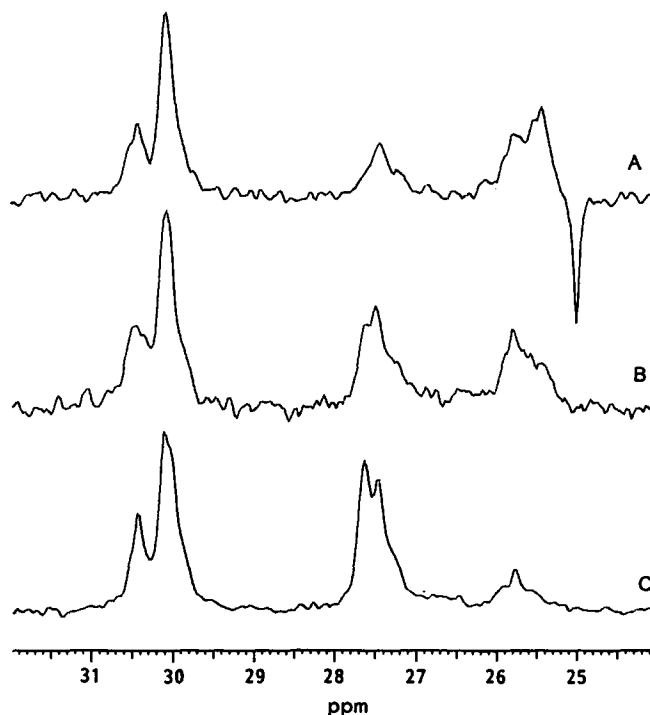

Figure 2 ^{13}C n.m.r. spectra for copolymers of methyl isopropenyl ketone with methyl methacrylate, prepared at 60°C using ^{13}C-AIBN. Values of [MIPK]/[MMA] in feed: A, 0.36; B, 1.09; C, 3.23
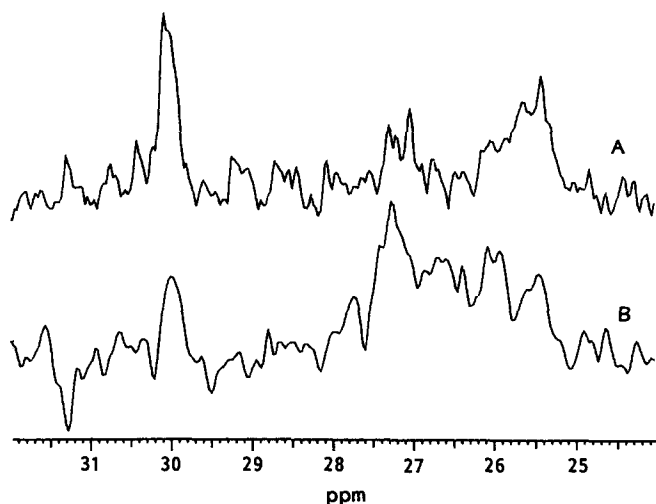
Figure 3 ^{13}C n.m.r. spectra for copolymers of methyl vinyl ketone with methyl methacrylate, prepared at 60°C using ^{13}C-AIBN. Values of [MVK]/[MMA] in feed: A, 0.44; B, 1.32

Table 1 Selected values of monomer reactivity ratios

Monomer 1	Monomer 2	r_1	r_2
MMA	MA	2.0	0.4
MMA	STY	0.5	0.5
MA	STY	0.15	0.8
MAN	AN	1.7	0.4
MAN	STY	0.3	0.4
AN	STY	0.1	0.4

MMA, methyl methacrylate
MA, methyl acrylate
STY, styrene
MAN, methacrylonitrile
AN, acrylonitrile

compare the numbers of initiator fragments attached to monomeric units of the two types, using the relationship[5]

$$\frac{\text{no. of R.MVK- end-groups}}{\text{no. of R.MMA- end-groups}} = \frac{B - A}{2A}$$

where A is the area covered by the peak at $\delta \approx 30.2$ ppm and B is the area covered by the remaining end-group signals. For copolymers for systems for which [MVK]/[MMA] had values of 0.44 and 1.32, the values of (no. of R.MVK- end-groups)/(no. of R.MMA- end-groups) are 1.1 and 3.2, respectively, leading to values of $k_{MVK}/k_{MMA} = 2.5$ and 2.4; in view of the difficulties, the close agreement between the results must be regarded as fortuitous. It appears that both MVK and MIPK are appreciably more reactive than MMA towards the 1-cyano-1-methylethyl radical and that $k_{MVK}/k_{MIPK} = 1.7$ at 60°C.

It is interesting to consider generally the effects of introducing an α-methyl group into a monomer, not only upon the reactivity of the monomer itself but also upon that of the conjugate polymer radical. In principle there is a straightforward established procedure for comparison of the reactivities of monomers towards a particular polymer radical, using monomer reactivity ratios for appropriate copolymerizations. Suppose that the reference polymer radical $(P_A.)$ is derived from monomer A and that reactivity ratios are known for the copolymerizations of A (monomer 1) with monomers B and C. The growth reactions involving $P_A.$ with A, B and

C are given velocity constants k_{AA}, k_{AB} $(= k_{AA}/r_{1(AB)})$ and K_{AC} $(= k_{AA}/r_{1(AC)})$, respectively; their relative values are therefore 1, $1/r_{1(AB)}$ and $1/r_{1(AC)}$.

Comparisons are made here between the reactivities of the members of the pairs (methyl acrylate)/MMA and acrylonitrile/methacrylonitrile towards polymer radicals. The reactivity ratios used for this purpose are contained in *Table 1* and can be regarded as reasonable on the basis of values given in a collection[6]. At present, there are insufficient data for an extension of the treatment to the pair MVK/MIPK. From the results in *Table 2*, it is evident that the velocity constants for the reactions of a polymer radical with monomers $CH_2:CHX$ and $CH_2:C(CH_3)X$, where X is $COOCH_3$ or CN, do not differ by a factor greater than 2.5 in any of the cases considered; in none of the examples is the monomer $CH_2:CHX$ more reactive than $CH_2:C(CH_3)X$. The results from studies of end-groups (*Table 3*) show that introduction of an α-methyl group into a monomer does not have a large effect upon reactivity towards the 1-cyano-1-methylethyl radical; in this case, there is only one example of the monomer $CH_2:C(CH_3)X$ being more reactive than $CH_2:CHX$.

Attack of a radical on a monomer occurs almost exclusively at the unsubstituted end of the double bond (i.e. tail-addition) for the systems considered here so that it is unlikely that introduction of an α-methyl group into the monomer would cause serious interference with the addition. This consideration may not apply, however, to the reactions of the polymer radicals $P.CH_2.CHX.$ and $P.CH_2.C(CH_3)X.$ with a particular monomer since the methyl group is at a position where it might cause some shielding of the reactive centre. It is significant in this connection that there is a tendency for some highly substituted mohomers, notably esters of methacrylic acid, to give predominantly syndiotactic polymers in radical polymerization even at quite high temperatures; the effect is reasonably attributed to some steric control of the

Table 2 Comparisons of velocity constants for growth reactions in radical polymerizations at 60°C

Polymer radical	Monomer A	Monomer B	(k for radical + M_A)/ (k for radical + M_B)
PolyMMA	MMA	MA	2/1
PolyMA	MMA	MA	2.5/1
PolySTY	MMA	MA	1.6/1
PolyMAN	MAN	AN	1.7/1
PolyAN	MAN	AN	2.5/1
PolySTY	MAN	AN	1/1

Table 3 Reactivities of monomers $CH_2:CHX$ and $CH_2:C(CH_3)X$ towards the 1-cyano-1-methylethyl radical

Substituent X in monomer	Relative reactivity towards radical[a]		
	$CH_2:CHX$	$CH_2:C(CH_3)X$	References
CN	0.79	0.61	7, 5
C_6H_5	1.79	1.69	5, 8
$COCH_3$	2.4	1.4	This work
$COOC_2H_5$	0.6	1.00[b]	9

[a] Relative reactivity of MMA taken as 1.00
[b] Comparison made between ethyl acrylate and MMA. It is known[10] that the methyl and ethyl esters of methacrylic acid have very similar reactivities towards the reference radical

Table 4 Values of velocity constant for various growth reactions in radical polymerizations

Polymer radical	Monomer	k (mol^{-1} dm^3 s^{-1})
MMA	MMA	730
MA	MMA	5225
MMA	MA	365
MA	MA	2090
MMA	STY	1460
MA	STY	13 900
MAN	MAN	200
AN	MAN	6150
MAN	AN	120
AN	AN	2460
MAN	STY	670
AN	STY	24 600

growth reactions, perhaps including an influence of the penpenultimate unit in the reacting radical[11].

Jenkins[12] pointed out that steric effects are commonly assumed to be negligible in reactions involving monomers substituted at only one end of the double bond. He suggested that the assumption is justified by the success of the 'Q and e'[13] and 'patterns of reactivity'[14] treatments. He stated, however, that the reluctance of most 1,2-disubstituted monomers to engage in polymerization can be attributed to steric effects; it should be noted that the readiness with which acenaphthylene enters into radical polymerization is associated with strain in the monomer and its relief by the opening of the ethylenic double bond. Hoyland[15] has admitted that the various treatments designed to calculate monomer reactivity ratios and to treat them theoretically are subject to certain limitations, which include neglect of penultimate effects and also exclusion of those reactions in which steric effects are of considerable importance. It is now suggested that steric effects may be quite pronounced for the reactions of the polymer radicals corresponding to monomers $CH_2:C(CH_3)X$.

The reactivities of polymer radicals towards a reference monomer can be compared by using monomer reactivity ratios for the various copolymerizations, but it is necessary also to know the values of k_p for the homopolymerizations involving the radicals under consideration. The requirement to have information on k_p imposes a severe limitation since this quantity is known for so few monomers. Suppose that polymer radicals P_A. and P_B. are to be compared in their reactions with monomer C. The reactions are given velocity constants k_{AC} and k_{BC}, respectively; the reactivity ratio $r_{1(AC)}$ for the copolymerization of M_A (monomer 1) with M_C is given by k_{AA}/k_{AC}, so that $k_{AC}=k_{AA}/r_{1(AC)}$ and similarly $k_{BC}= k_{BB}/r_{1(BC)}$.

The present comparisons concern, first, the polymer radicals derived from MMA and methyl acrylate (MA) in reactions with the monomers MMA, MA and STY and, secondly, the polymer radicals corresponding to methacrylonitrile (MAN) and acrylonitrile (AN) with MAN, AN and STY. Following Jenkins[12], values of k_p at 60°C for MMA, MA, MAN and AN are taken as 730, 2090, 200 and 2460 mol^{-1} dm^3 s^{-1}, respectively; the reactivity ratios are shown in *Table 1* and the results of the calculations in *Table 4*. Significance cannot be attached to

the precise values shown in column 3 of *Table 4* but, plainly, for each of the six comparisons, the polymer radical derived from $CH_2:C(CH_3)X$ is less reactive than the radical corresponding to the monomer $CH_2:CHX$; the differences are considerably greater than those in *Table 2* and in the opposite sense. The results are consistent with the view that the α-methyl group in the polymer radical interferes to an appreciable extent in the reactions of the radical with monomers.

Another of the indications of steric effects due to the methyl group in polymer radicals comes from studies of copolymerizations involving *trans*-stilbene. Incorporation of stilbene into polymers in most cases is very limited but it is appreciably greater for $CH_2:CHX$ than for $CH_2:C(CH_3)X$ when X is CN[7], $COOCH_3$[16], C_6H_5 or $COCH_3$[17]. Using values of k_p quoted above, the velocity constants for the reactions of the polyAN and polyMAN radicals with stilbene at 60°C are 1230 and 1.5 mol^{-1} dm^3 s^{-1}, respectively, and, for the corresponding reactions of the polyMA and polyMMA radicals, they are 536 and 1.7 mol^{-1} dm^3 s^{-1}, respectively. The only reasonable explanation for the large differences seems to be based on steric hindrance caused by the methyl group.

A subsequent paper will contain further and more detailed discussion of the effects of methyl groups on the reactivities of monomers and polymer radicals.

ACKNOWLEDGEMENTS

REFERENCES

1 Coleman, Jr, L. E. and Meinhardt, N. A. *Fortschr. Hochpolym. Forsch.* 1959, 1, 159
2 Lyons, A. R. *J. Polym. Sci., Macromol. Rev.* 1972, 6, 251
3 Weir, N. A., Whiting, K. and Arct, J. *Polym. Commun.* 1987, 28, 284
4 Bevington, J. C., Ebdon, J. R. and Huckerby, T. N. *Eur. Polym. J.* 1985, 21, 685
5 Bevington, J. C., Huckerby, T. N. and Hutton, N. W. E. *J. Polym. Sci., Polym. Chem. Edn.* 1982, 20, 2655
6 Young, L. J. in 'Polymer Handbook', 2nd Edn (Eds J. Brandrup and E. H. Immergut), Wiley–Interscience, New York, 1975, pp. II–105
7 Barson, C. A., Bevington, J. C. and Huckerby, T. N. *Polym. Bull.* 1986, 16, 209
8 Behari, K., Bevington, J. C. and Huckerby, T. N. *Makromol. Chem.* 1987, 188, 2441
9 Bevington, J. C., Huckerby, T. N. and Hutton, N. W. E. *Eur. Polym. J.* 1984, 20, 525
10 Behari, K., Bevington, J. C. and Huckerby, T. N. in preparation
11 Moad, G., Solomon, D. H., Spurling, T. H., Johns, S. R. and Willing, R. I. *Aust. J. Chem.* 1986, 39, 43
12 Jenkins, A. D. in 'Reactivity, Mechanism and Structure in Polymer Chemistry' (Eds A. D. Jenkins and A. Ledwith), Wiley, London, 1974, Ch. 4
13 Alfrey, T. and Price, C. C. *J. Polym. Sci.* 1947, 2, 101
14 Bamford, C. H., Jenkins, A. D. and Johnston, R. *Trans. Faraday Soc.* 1959, 55, 418
15 Hoyland, J. R. *J. Polym. Sci. A-1* 1970, 8, 885
16 Barson, C. A. and Bevington, J. C. *Eur. Polym. J.* 1987, 23, 251
17 Barson, C. A., Behari, K. and Bevington, J. C. *Polym. Bull.* 1987, 18, 265