

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

THE COPOLYMERIZATION ACTIVITY OF SOME VINYL ETHERS

J. C. Bevington^a; T. N. Huckerby^a; A. D. Jenkins^b

^a School of Physics & Chemistry, University of Lancaster, Lancaster, La., U.S.A. ^b School of Chemistry, Physics & Environmental Science, University of Sussex, Brighton, Sussex, U.K.

Online publication date: 12 June 1999

To cite this Article Bevington, J. C. , Huckerby, T. N. and Jenkins, A. D.(1999) 'THE COPOLYMERIZATION ACTIVITY OF SOME VINYL ETHERS', *Journal of Macromolecular Science, Part A*, 36: 12, 1907 – 1922

To link to this Article: DOI: 10.1081/MA-100101633

URL: <http://dx.doi.org/10.1081/MA-100101633>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE COPOLYMERIZATION ACTIVITY OF SOME VINYL ETHERS

J. C. Bevington and T. N. Huckerby

School of Physics & Chemistry
University of Lancaster
Lancaster, Lancs., LA1 4YA, U.K.

A. D. Jenkins*

School of Chemistry
Physics & Environmental Science
University of Sussex
Brighton, Sussex, BN1 9QJ, U.K.

Key Words: Radical Copolymerization, Vinyl Ethers, Methyl Methacrylate, Patterns of Reactivity

ABSTRACT

Monomer reactivity ratios have been determined for the radical copolymerizations of several vinyl ethers with either styrene or methyl methacrylate. The results permit some general conclusions to be drawn regarding the reactivities of the vinyl ethers, $\text{CH}_2=\text{CH.O.R}$. When R is a comparatively small alkyl group, the reactivity of the vinyl ether towards the poly(methyl methacrylate) radical is low and almost independent of the precise nature of R; the reactivity is much lower when R is $-\text{CH}_2.\text{CH}_2.\text{Cl}$ and also when R is a fairly large alkyl group, such as $-\text{C}_{12}\text{H}_{25}$, or an oxyethylene chain such as $-\text{CH}_2.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_2.\text{OH}$.

* Author to whom correspondence should be addressed.

INTRODUCTION

The examination of end-groups in polymers and copolymers made using either benzoyl peroxide or 2,2'-azobisisobutyronitrile (AIBN) as initiator has revealed that vinyl ethers are very reactive towards the oxygen-centred benzoyloxy radical but rather unreactive towards the carbon-centred 2-cyano-2-propyl radical [1]. The radical derived from AIBN is a model for the polymethacrylonitrile (PMAN) radical and so the results of the studies of end-groups are consistent with the view that the vinyl ethers are generally unreactive in radical copolymerizations with monomers such as MAN. The limited information available on monomer reactivity ratios for copolymerizations of methyl methacrylate (MMA) or styrene (STY), taken as monomer-1, with various vinyl ethers (taken as monomer-2) has been collected from a variety of sources. If results for some cresyl vinyl ethers [2] are excluded, all values of r_1 exceed 10 (greatly so in some cases), indicating low reactivities of the vinyl ethers towards the carbon-centred polyMMA and polySTY radicals; the quoted values of r_2 are close to zero. When monomer-1 is acrylonitrile, almost all the reported values of r_1 are close to unity while those of r_2 are again very small because of the reluctance of a poly(vinyl ether) radical to react with a vinyl ether monomer [2].

For several of the vinyl ethers, sufficient monomer reactivity ratio data have been collected by Greenley [2] to permit evaluation of their u , v and π parameters by the procedures described elsewhere [3] with the results displayed in Table 1. (The u , v and π parameters are reactivity characteristics in the Revised Patterns Scheme which are the counterparts of Q and e in the Alfrey-Price treatment of binary copolymerization.) Compared with most of the vinyl monomers for which parallel data are available, the u values are rather unusual in being positive, or only slightly negative, except for the phenyl-substituted compound; this presumably reflects the influence of the oxygen atom adjacent to the vinyl group. The mean values for the first six listed monomers are: $u = 0.515$; $v = -1.672$; and $\pi = 0.170$.

A report is now given of a survey of the involvement in radical copolymerizations with MMA at 60°C of vinyl ethers ($\text{CH}_2\text{:CH.O.R}$) of two types, viz., some in which R is comparatively small and compact, and others in which R is either a relatively large hydrocarbon group or an oxyethylene chain. STY was used instead of MMA in a few cases. The vinyl ethers considered were:

group (a)

n-propyl vinyl ether (NPVE)	R = -CH ₂ .CH ₂ .CH ₃
<i>tert</i> -butyl vinyl ether (TBVE)	-C(CH ₃) ₃
cyclohexyl vinyl ether (CHVE)	-cycloC ₆ H ₁₁
2-chloroethyl vinyl ether (CEVE)	-CH ₂ .CH ₂ .Cl

group (b)

dodecyl vinyl ether (DDVE)	-n-C ₁₂ H ₂₅
octadecyl vinyl ether (ODVE)	-n-C ₁₈ H ₃₇
ethylene glycol vinyl ether (EGVE)	-CH ₂ .CH ₂ .OH
diethylene glycol vinyl ether (DEGVE)	-CH ₂ .CH ₂ .O.CH ₂ .CH ₂ .OH
triethylene glycol methyl vinyl ether (TEGMVE)	-CH ₂ .CH ₂ .O.CH ₂ .CH ₂ .O.CH ₂ .CH ₂ .O.CH ₃

Experiments were also performed with two divinyl ethers (CH₂:CH.O.R'.O.CH:CH₂), viz.,

ethylene glycol divinyl ether (EGDVE)	-R' = -CH ₂ .CH ₂ -
triethylene glycol divinyl ether (TEGDVE)	-R' = -CH ₂ .CH ₂ .O.CH ₂ .CH ₂ .O.CH ₂ .CH ₂ -

TABLE 1. u , v and π Parameters for Some Vinyl Ethers and Reference Monomers

Monomer	u	v	π
Vinyl ethyl ether	1.18	-2.03	0.192
Vinyl n-butyl ether	-0.076	-1.31	0.162
Vinyl iso-butyl ether	-0.542	-1.07	0.235
Vinyl 2-chloroethyl ether	1.18	-2.06	0.105
Vinyl octyl ether	0.723	-1.81	0.162
Vinyl dodecyl ether	0.623	-1.75	0.162
Divinyl ether	1.13	-1.44	0.008
Vinyl phenyl ether	-2.24	-0.16	0.685
Styrene	0	0	0
Methyl methacrylate	-1.18	0.23	0.339
Acrylonitrile	-2.60	0.42	0.701

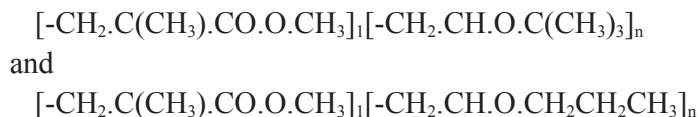
There is interest in certain resins derived from unsaturated esters and vinyl ethers; they yield crosslinked materials on exposure to light. In this connection, triethylene glycol divinyl ether has been examined as a donor-monomer in copolymerizations with dialkyl fumarates as acceptor-monomers. It appears that charge-transfer complexes can be formed and that photo-copolymerizations may occur, even in the absence of added initiator [4].

EXPERIMENTAL

MMA, STY, and AIBN were purified by standard procedures. Benzene used as diluent for most of the polymerizations was HPLC grade (Aldrich); other solvents were of reagent grade. ODVE (Lancaster Synthesis) was used as received; other vinyl ethers (Aldrich) were distilled, and their identities and purities were confirmed by GC/MS and/or ^{13}C NMR.

Polymerizations involved MMA at 3.15 mol dm^{-3} with AIBN at $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ or STY at 4.16 mol dm^{-3} with AIBN at $3.00 \times 10^{-2} \text{ mol dm}^{-3}$; the total volume of each reaction system was close to 3.0 mls. Reactions were performed at 60°C under anaerobic conditions and were monitored by dilatometry; no inhibition was observed and the contraction vs. time plots were linear. Conversions did not exceed 10% of the principal monomer. Polymers were recovered by precipitation in methanol, purified by second precipitations from solutions in toluene, and finally dried in vacuum to constant weight.

Compositions of copolymers were found from 400 MHz ^1H NMR spectra recorded for solutions in CDCl_3 using a JEOL GSX-400 spectrometer. When the principal monomer was MMA, the spectral area (A_a) for signals near 3.6 ppm was compared with the area (A_b) for signals between 0.6 and 2.2 ppm; Figure 1 shows an example of such a spectrum. Area A_a corresponds to hydrogen atoms attached to carbon atoms adjacent to oxygen or chlorine atoms; area A_b refers to hydrogen atoms attached to carbon atoms not adjacent to oxygen or chlorine atoms. Thus, consider copolymers of MMA with TBVE or NPVE, represented respectively as



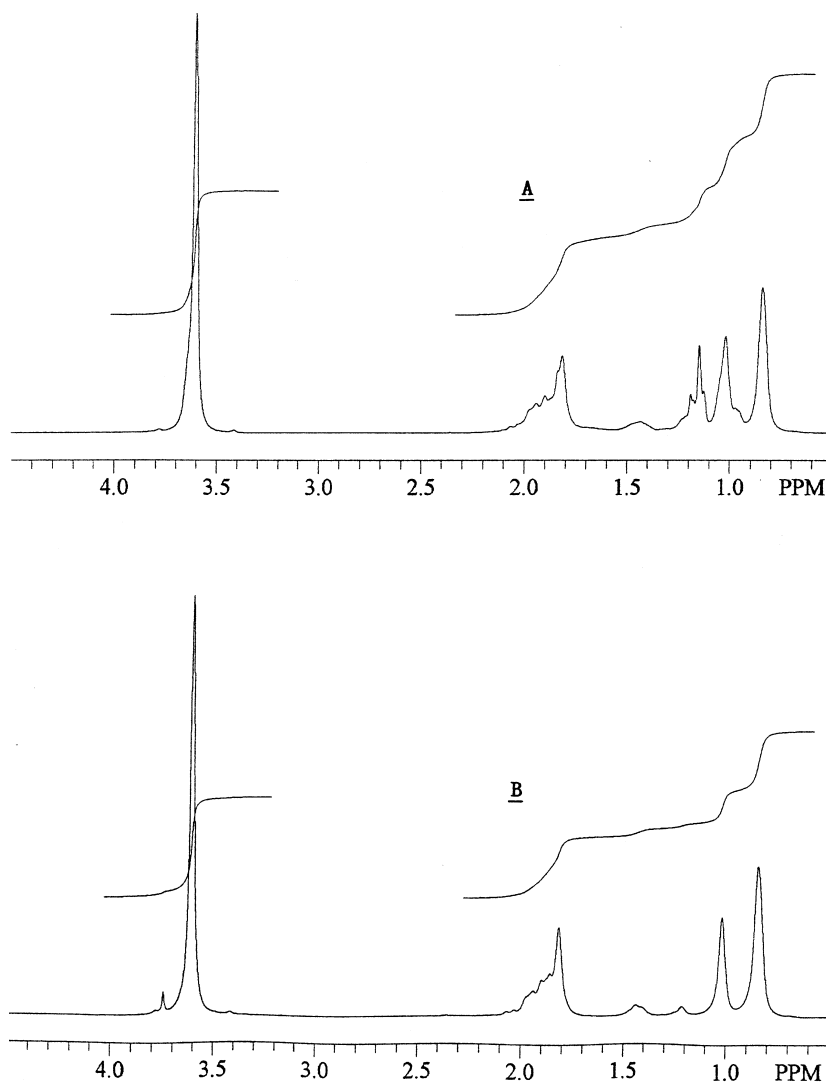


Figure 1. A. Part of the 400 MHz ¹H NMR spectrum of a copolymer of MMA with TBVE. [MMA]/[TBVE] in feed = 2.47. [MMA]/[TBVE] in copolymer found as 10.3; B. Reference spectrum of poly(methyl methacrylate) prepared similarly but from a system containing no vinyl ether. In both cases, the integrals are shown.

For the former, $A_a/A_b = (3+n)/(5+ln)$ and, for the latter, $A_a/A_b = (3+3n)/(5+7n)$. An integrated spectrum gives a value for A_a/A_b and so n can be calculated.

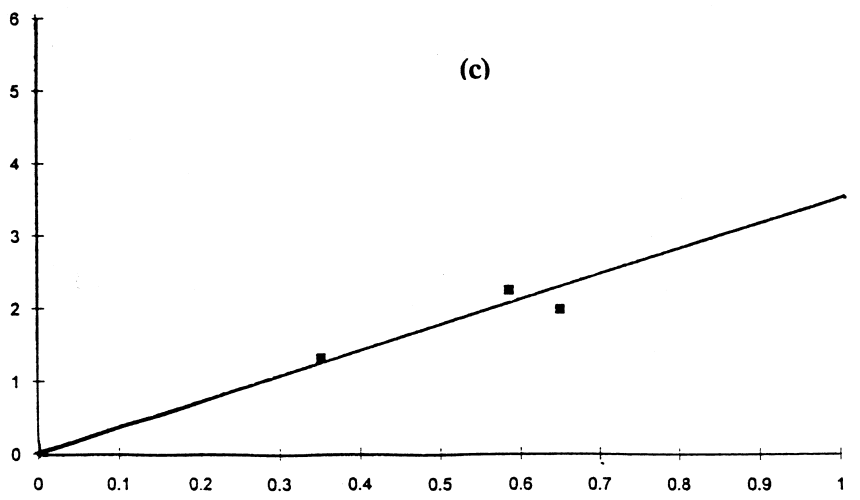
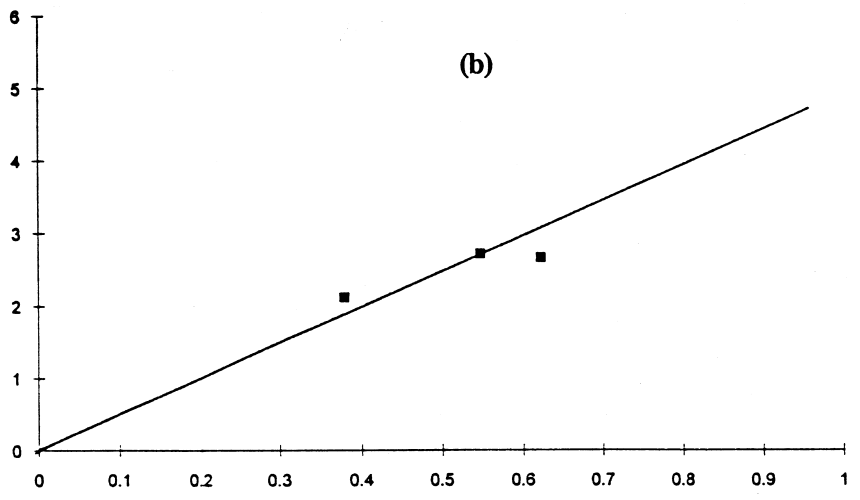
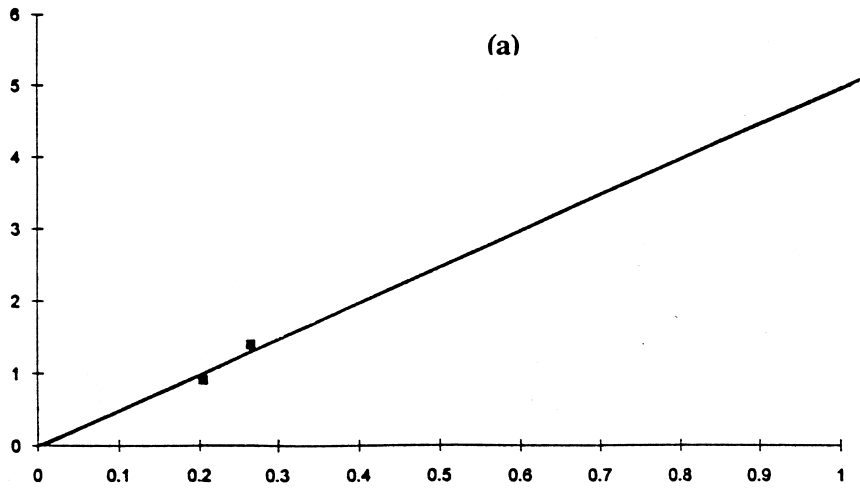
This method for analysis cannot be applied to cases such as MMA with ethyl vinyl ether because the ratio of the numbers of hydrogen atoms contributing to areas A_a and A_b is the same for both types of monomeric unit. The procedure is not very satisfactory for copolymers of MMA with NPVE since the ratio of the numbers of the two types of hydrogen atoms has rather similar values for the two monomeric units. In one of the actual cases, A_a/A_b for a copolymer containing NPVE was found to be 1.73 leading to n being 0.105; if A_a/A_b had been shifted to 1.72 or to 1.74, n would have been 0.087 or 0.123 i.e. variations approaching 20%. For the monomeric units derived from the other vinyl ethers considered here, the ratios of the numbers of hydrogen atoms contributing to the areas A_a and A_b are very different from that for MMA units, so that the value found for n are less sensitive to small variations in A_a/A_b .

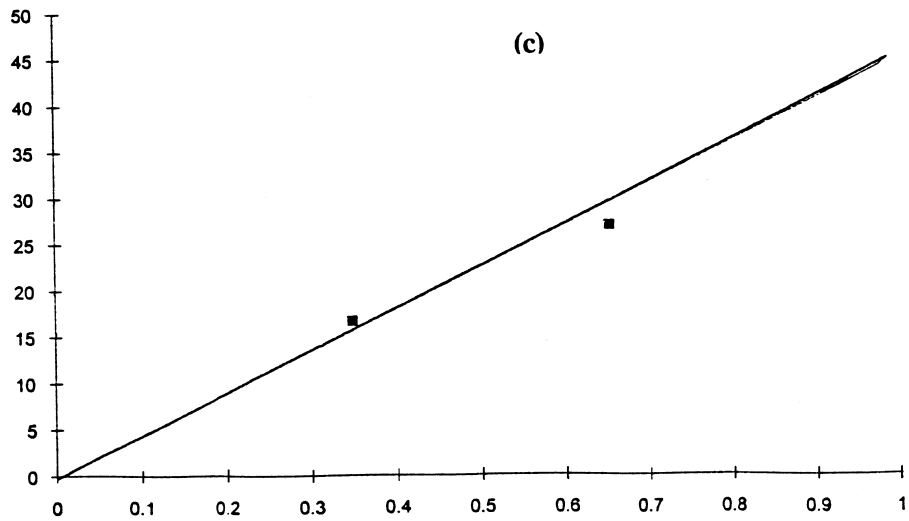
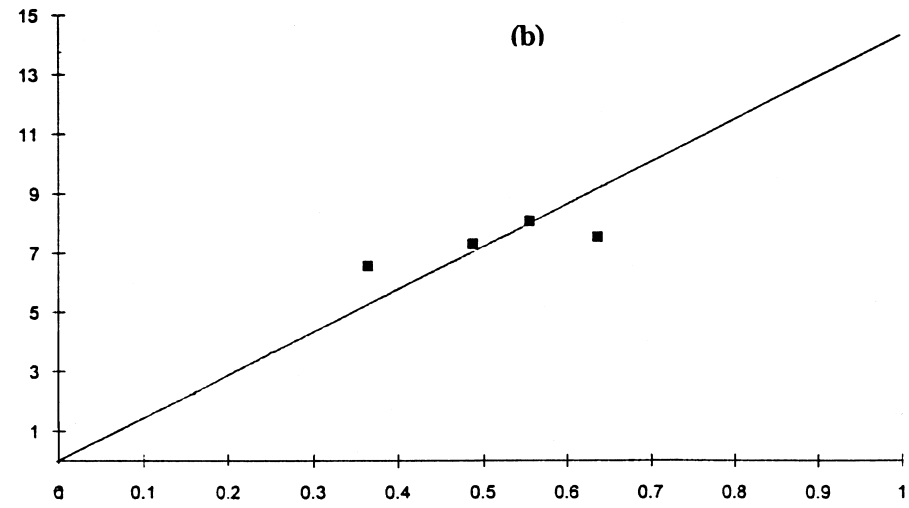
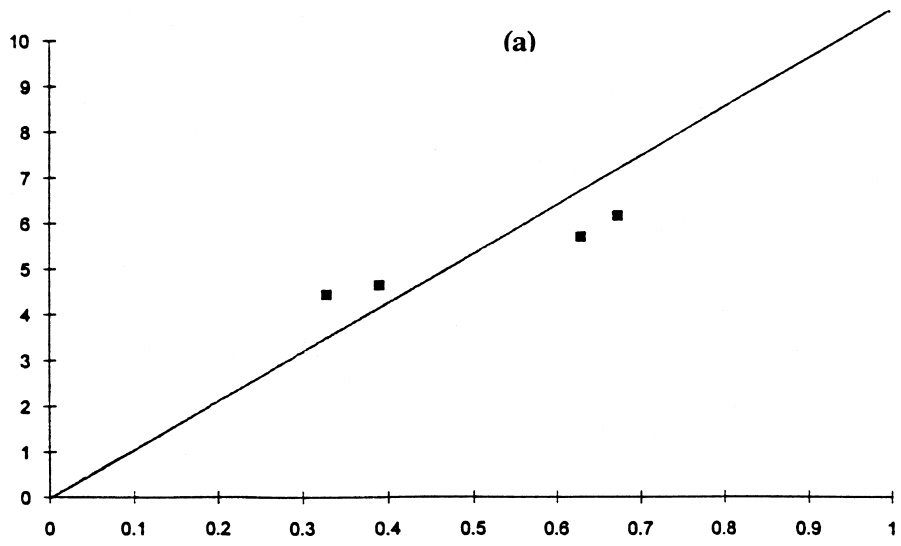
The procedure adopted for analyses of the few copolymers of STY with vinyl ethers depended upon comparison of the spectral area (A_c) for "aromatic" hydrogens (6.0-7.5 ppm) with that (A_d) for "aliphatic" hydrogens (1.0-2.4 ppm). A copolymer of STY with DDVE, for example, can be represented as $[-CH_2.CH(C_6H_5)-]_1[-CH_2CH.O.C_{12}H_{25}-]_n$ so that $A_c/A_d = 5/(3 + 28n)$. This method is not sufficiently reliable since it amounts to measuring the small changes in STY contents resulting from the incorporation of minor amounts of vinyl ethers. The mean values of M_n for the polymers made using MMA were in the region of 115,000 and those for polymers made with STY were about 20,000. The contents of initiator fragments forming end-groups were therefore small enough for them to be neglected in the calculations.

RESULTS AND DISCUSSION

Results for copolymerizations of MMA with NPVE, CHVE or TBVE are shown in Figure 2 and those with DDVE, ODVE or CEVE in Figure 3. There is

Figure 2. Kelen-Tüdös plots for the copolymerizations of methyl methacrylate with (a) *n*-propyl vinyl ether, (b) cyclohexyl vinyl ether, or (c) *tert*-butyl vinyl ether. Abscissa: ξ ; ordinate: η .





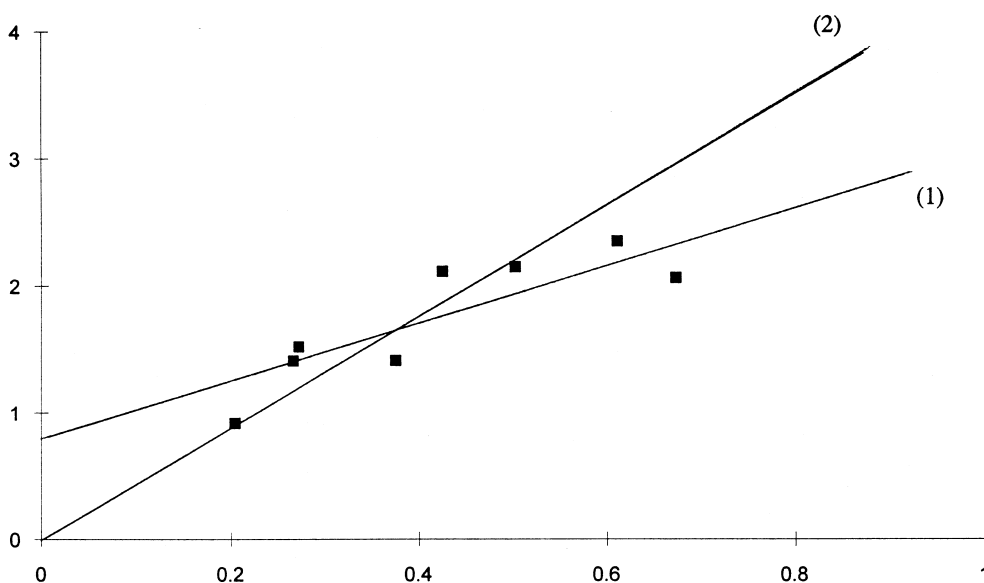


Figure 4. Combined Kelen-Tüdös plot for the separate copolymerizations of methyl methacrylate with *n*-propyl vinyl ether, cyclohexyl vinyl ether, and *tert*-butyl vinyl ether. Abscissa: ξ ; ordinate: η .

considerable scatter among the points and it would be necessary to refine experimental techniques and to obtain more results if more precise values of monomer reactivity ratios were to be obtained. It is evident, however, that there are very great differences between the behaviors of the vinyl ethers referred to in Figure 2 and those of the ethers considered in Figure 3, in the sense that the latter are incorporated to much smaller extents on a molar basis. If no distinction is made between NPVE, TBVE and CHVE, a single Kelen-Tüdös plot [5] can be drawn to represent the behavior of the family of simple alkyl-substituted vinyl ether monomers. Line 1 in Figure 4 corresponds to the linear least-squares analysis of all the points, equally weighted; it gives a positive intercept on the $\xi = 0$ axis, which is unacceptable. In view of the small number of points and the somewhat

Figure 3. Kelen-Tüdös plots for the copolymerizations of methyl methacrylate with (a) dodecyl vinyl ether, (b) octadecyl vinyl ether, or (c) 2-chloroethyl vinyl ether. Abscissa: ξ ; ordinate: η .

TABLE 2. Values of r_1 for Copolymerizations of MMA (Monomer 1) with Vinyl Ethers (Monomer 2). Note That, in All Cases, r_2 Is Close to 0

Monomer	r_1
n-propyl vinyl ether (NPVE)	3.5
<i>tert</i> -butyl vinyl ether (TBVE)	3
cyclohexyl vinyl ether (CHVE)	4.5
2-chloroethyl vinyl ether (CEVE)	43
dodecyl vinyl ether (DDVE)	10
octadecyl vinyl ether (ODVE)	14
ethylene glycol vinyl ether (EGVE)	16
diethylene glycol vinyl ether (DEGVE)	19
triethylene glycol methyl vinyl ether (TEGMVE)	16
ethylene glycol divinyl ether (EGDVE)	4
triethylene glycol divinyl ether (TEGDVE)	6

broad scatter, the rigorous use of the least-squares approach is not justified; line 2 is drawn by eye so as to pass through the origin and, from this, it appears that r_1 and r_2 are in the regions of 4 and 0, respectively; for DDVE, ODVE and CEVE, r_2 is zero in all cases while r_1 has values of approximately 10, 14, and 43, respectively. The monomer reactivity ratios for all the monomers studied are collected in Table 2.

The method of analysis of copolymers of STY with vinyl ethers was not reliable for reasons already explained. Nevertheless, comparison of results in Table 3 with those in Figures 2 and 3 confirms that, for STY as monomer-1, values of r_1 must be substantially greater than those for the corresponding cases involving MMA. This is precisely what would have been expected on the basis of the mean u , v and π values reported above for typical vinyl ethers; if these parameters are substituted into the basic Patterns Equation,

$$\log r_1 = \log r_{1S} - u_2 \pi_1 - v_2$$

TABLE 3. Copolymerizations of Styrene with Vinyl Ethers

<u>vinyl ether</u>	<u>[STY]/[vinyl ether] in feed</u>	<u>[STY]/[vinyl ether] in copolymer</u>
NPVE	1.6	31
TBVE	4.6	49
CHVE	2.5	62
DDVE	1.9	113

with either styrene or methyl methacrylate as monomer 1, the predicted values of r_1 are 47 for STY and 14.5 for MMA, very much in line with the trend of the values found here. The value of k_p for the homopolymerization of STY is appreciably less than that for MMA and so the rate constants for the reactions of a polySTY radical with these vinyl ethers must be much less than those for the similar reactions of a polyMMA radical.

The possibility that the nature of the diluent used in the polymerizing system might profoundly affect the characteristics of the copolymerizations was tested for cases in which [MMA] and [DDVE] in the initial feed were 3.15 and 0.51 mol dm⁻³, respectively, and in which benzene, dimethylformamide and dimethylsulfoxide were in turn used as diluent. Only small differences were found between the compositions of the resulting copolymers, the values of [MMA]/[DDVE] being 56, 54, and 58, respectively.

The copolymers of MMA with the vinyl ethers were isolated and purified by precipitation in methanol, a process which yields the materials in very convenient forms but which fails to recover the smallest polymer molecules; more complete recovery is achieved by precipitation in hexane [6]. The possibility that the "fractionation" accompanying precipitation in methanol might have a significant effect on the compositions of the copolymers was eliminated by consideration of the results for a copolymerization in which the molar ratio [MMA]/[DDVE] in the feed was 2.47. Part of the polymerized system was treated with methanol and part with hexane; the values of [MMA]/[DDVE] in the resulting samples of copolymers were almost identical at 30.4 and 30.7.

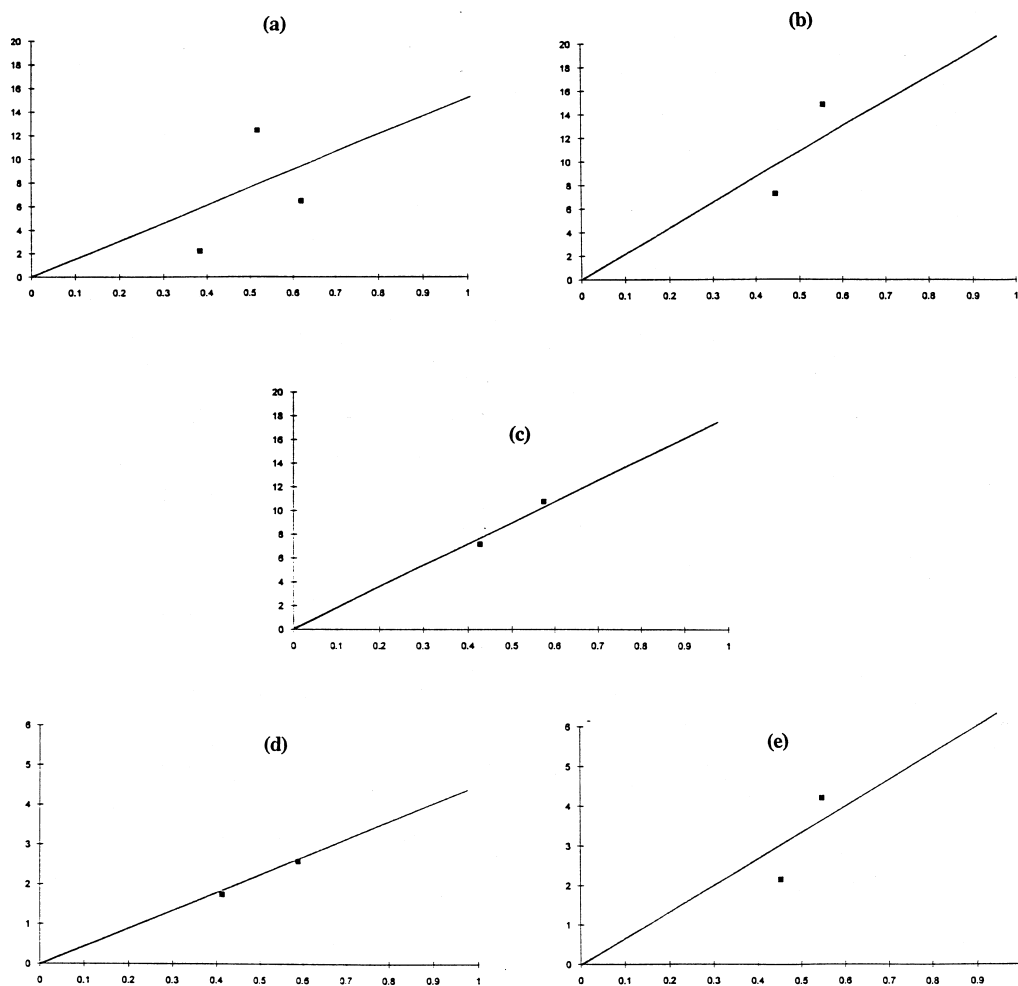


Figure 5. Kelen-Tüdös plots for the copolymerizations of methyl methacrylate with (a) ethylene glycol vinyl ether; (b) diethylene glycol vinyl ether; (c) triethylene glycol vinyl ether; (d) ethylene glycol divinyl ether; or (e) triethylene glycol divinyl ether. Abscissa: ξ ; ordinate: η .

Figure 5 refers to copolymers of MMA with vinyl ethers of the general formula $\text{CH}_2\text{:CH.O.}[\text{CH}_2\text{CH}_2\text{O}]_n\text{X}$, where X- is -H or $-\text{CH}_3$ and n is 1, 2 or 3. Plainly, these vinyl ethers resemble DDVE and ODVE in that they enter the copolymers much less readily than those considered in Figure 2. It is not possible to be sure of significant differences between the extents of incorporation of

EGVE, DEGVE and TEGVME at the same molar concentration in the feed but Kelen-Tüdös plots suggest that, for each of the compounds, $r_2 = 0$ and that the values of r_1 are 14, 19, and 16, respectively.

Figure 5 includes results for the divinyl ethers EGDVE and TEGDVE, for which $r_2 = 0$ and $r_1 = 4$ and 6, respectively; they are incorporated to greater extents than the mono-compounds. For a particular value of $[MMA]/[\text{divinyl ether}]$ in the feed, the value of $[MMA]/[\text{vinyl ether}]$ in the copolymer is considerably less than that for the corresponding monovinyl ether. This result is as expected because the two carbon-carbon double bonds in EGDVE and TEGDVE must have very similar reactivities and they must resemble those of the double bonds in the corresponding monovinyl ethers. There are substantial differences between the values of r_1 for the vinyl ethers having small and compact alkyl groups and those for others having long n-alkyl groups, those bearing oxyethylene groups, and CEVE. The lower reactivities towards the poly(methyl methacrylate) radical of EGVE, DEGVE, TEGMVE and CEVE might be due to the replacement of alkyl groups by more polar moieties but an explanation of this type could not be applied to account for the lower reactivities of DDVE and ODVE. It is now suggested that coiling of the long alkyl chains might lead to interference with the reactions of the vinyl ethers with PMMA radicals. It should be noted that comments have been made on the values of k_p for the homopolymerization of methacrylic esters having alkyl groups of very different sizes [7, 8]. It was suggested that the differences could not be attributed to electronic or polar effects but that they could arise from the longer alkyl chains being so positioned that they shield or otherwise affect the radical centres. The case of vinyl ethers such as DDVE is rather different because the rather weak tendencies to copolymerize with MMA must be associated with characteristics of the monomers, not those of the corresponding polymer radicals. At one time an explanation for the differences between the reactivities of, say, TBVE and DDVE would have been sought in terms of the differential effects of the alkyl groups in stabilizing the poly(vinyl ether) radicals formed by copolymerization: according to Moad and Solomon [9], however, the current view is that the rates of growth reactions may be less influenced by thermodynamic considerations than by kinetic factors, including steric interference.

It is necessary to consider the natures of the EGDVE and TEGDVE units in the copolymers. There could be carbon-carbon double bonds at the ends of pendant oxyethylene chains which would be available for subsequent growth, leading to branched polymer molecules and ultimately to cross-linking; the low

reactivities of the vinyl ethers would mean that these branching and crosslinking processes would not occur readily. On the other hand, incorporation of a divinyl ether unit might be followed by reaction of the resulting radical with its own second olefinic group, leading to cyclopolymerization. This process would result in a 12- or 13-membered ring in the case of TEGDVE and in a 6- or 7-membered ring for EGDVE. For the copolymerizations of MMA with vinyl ethers in general, the monomer reactivity ratios indicate that the reaction of a poly(vinyl ether) radical with a vinyl ether monomer is unlikely to compete effectively with the reaction of the radical with MMA. This argument would be applicable not only for a monomer completely separate from the radical but also for a monomer attached to the radical through an oxyethylene chain, suggesting that cyclopolymerization is improbable for EGDVE or TEGDVE. It appears, however, that cyclopolymerization can occur under some circumstances. It has been reported that EGDVE and the divinyl derivative of diethylene glycol engage in cyclopolymerization [10]. The cationic polymerization of the divinyl ether of tetraethylene glycol has been found to result in a lightly cross-linked material which contains either [16]-crown-5 or perhaps [17]-crown-5 rings which could only have arisen from cyclopolymerization [11]. It is also relevant that an attempted cationic polymerization of the vinyl ether of tetraethylene glycol gave a cyclic acetal [11]; it must have been formed as a result of a coiling of the chain so that there could be a facile interaction between the functional groups at the two ends of the molecule.

Figure 5 includes results for systems in which the values of $[MMA]/[TEGDVE]$ in the initial feed were 9.7 and 22.5; the copolymers dissolved only slowly in $CDCl_3$. Another copolymerization for which the feed ratio was 3.8 led to a polymer which became swollen but did not dissolve in $CDCl_3$. These observations suggest that there is a real possibility of the copolymers containing side-chains with terminal unsaturation which can ultimately lead to crosslinking. The 1H NMR spectrum of the copolymer derived from the "[MMA]/[TEGDVE] = 9.7 system" contained very small signals at about 6 ppm, not observed in the spectra of copolymers derived from any of the monovinyl ethers. The additional signals may well originate from hydrogen atoms in $-CH:CH_2$ groups, suggesting the presence in the copolymer of TEGDVE units containing unreacted second vinyl ether groups; the size of the signals was insufficient for it to be supposed that each of the TEGDVE units was in this form. At this stage it is not possible to reach a firm conclusion concerning the occurrence of pendant unsaturation or of cyclic structures in copolymers of MMA with EGDVE or TEGDVE.

CONCLUSION

The vinyl ethers, $\text{CH}_2=\text{CH.O.R}$, show little tendency to undergo radical polymerization with methyl methacrylate (monomer 1) and even less with styrene; in all cases, r_2 is indistinguishable from zero. When R is a fairly small and compact alkyl group, r_1 is about 4.0.

The reactivity of the vinyl ether towards the poly(methyl methacrylate) radical is considerably reduced if a chlorine atom is introduced into R; thus, for 2-chloroethyl vinyl ether, r_1 is about 40. Values of r_1 of about 12 are found for vinyl ethers in which R is n-C₁₂H₂₅ or n-C₁₈H₃₇. For some of the vinyl ethers bearing oxyethylene chains, e.g. $\text{CH}_2=\text{CH.O.}[\text{CH}_2.\text{CH}_2.\text{O}]_n\text{X}$, where n is 1 or 3 and X is H or CH₃, r_1 is between 15 and 20. The divinyl ethers of polyethylene glycols can lead to crosslinking when used as comonomers with methyl methacrylate, and also to limited cyclopolymerization.

REFERENCES

- [1] J. C. Bevington, K. A. Dillingham, T. N. Huckerby, and B. J. Hunt, *J. Polym. Sci., Part A, Polym. Chem.*, **37**, 771 (1999).
- [2] R. Z. Greenley, *Polymer Handbook*, 3rd. Ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1989, p. II, 153.
- [3] A. D. Jenkins, *J. Polym. Sci., Part A, Polym. Chem.*, **37**, 113 (1999).
- [4] S. Katogi, C. W. Miller, C. E. Hoyle, and S. Jönsson, *Polymer*, **39**, 2709 (1998).
- [5] T. Kelen and F. Tüdös, *J. Macromol. Sci.*, **A9**, 1 (1975).
- [6] C. A. Barson, J. C. Bevington, and B. J. Hunt, *Eur. Polym. J.*, **32**, 1055 (1996).
- [7] R. A. Hutchinson, S. Beuerman, D. A. Paquet, Jr., and J. H. McMinn, *Macromolecules*, **30**, 3490 (1997).
- [8] M. D. Zammit, M. L. Coote, T. P. Davis, and G. D. Willett, *Macromolecules*, **31**, 955 (1998).
- [9] G. Moad and D. H. Solomon, *The Chemistry of Free Radical Polymerization*, Elsevier, Oxford, 1995, p. 4.
- [10] M. Biswas, A. Mazumdar, and P. Mitra, *Encyclopedia of Polymer Science & Engineering*, 2nd Ed., H. F. Mark, N. M. Bikales, and C. G. Overberger, Eds., Wiley, New York, 1989, p. 446.

- [11] L. J. Mathias and J. B. Canterberry, *Am. Chem. Soc., Polymer Preprints*, 22, 38 (1981).

Received April 20, 1999

Revision received June 20, 1999