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J. C. Bevington[a]; T. N. Huckerby[a]; B. J. Hunt[b]; A. D. Jenkins[c]
[a] School of Physics and Chemistry, Lancaster University, Lancaster, United Kingdom [b] Department of Chemistry, Lancaster University, Sheffield, United Kingdom [c] School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton, United Kingdom

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THE EFFECTS OF ALLYL ETHERS UPON RADICAL POLYMERIZATIONS

J. C. Bevington,[1],* T. N. Huckerby,[1] B. J. Hunt,[1],† and A. D. Jenkins[2]

[1]School of Physics and Chemistry, Lancaster University,
Lancaster LA1 4YA, United Kingdom
[2]School of Chemistry, Physics and Environmental Sciences,
University of Sussex, Brighton BN19QJ, United Kingdom

ABSTRACT

Three allyl ethers, viz. the ethyl, 2-hydroxyethyl and phenyl compounds, have been examined as additives in radical polymerizations of styrene (STY), methyl methacrylate (MMA) and acrylonitrile (ACN) at 60°C using azobisisobutyronitrile as initiator. As retarders and transfer agents, the ethers are considerably more effective with ACN than with the other monomers. Allyl phenyl ether engages in significant copolymerization with ACN and slight copolymerization with MMA; there is negligible incorporation in polySTY.

Key Words: Radical polymerization; Allyl ethers; Retardation; Transfer.

INTRODUCTION

Accounts have been given of the behavior of typical vinyl ethers in radical polymerizations [1, 2, 3]. Generally, they are rather unreactive towards carbon-centered radicals so that there is only limited incorporation when they are used as comonomers with, say, methyl methacrylate (MMA). The vinyl ethers react quite readily however, with oxygen-centered radicals such as benzoyloxy [1] and *tert*-butoxyl [4]. Certain vinyl ethers of only moderate complexity are effective transfer

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*Corresponding author.

†Present address: Department of Chemistry, Lancaster University, Sheffield S3 7HF, United Kingdom.

agents in radical polymerizations, acting by the addition-fragmentation mechanism [5]; it has been shown however that, if this process operates for simple vinyl ethers such as the n-propyl compound, the fragmentation is an inefficient process [3].

The examination of unsaturated ethers has now been extended to some allyl ethers $CH_2\mathbf{:}CH\cdot CH_2\cdot OR$ (R- = $-CH_2\cdot CH_3$, $-CH_2\cdot CH_2OH$ or $-C_6H_5$) used in conjunction with MMA, styrene (STY), or acrylonitrile (ACN). These monomers were selected for study, as being well suited for application of the new procedure for correlating and predicting reactivities in copolymerizations and transfer processes [6]. It might be expected that the allyl ethers would be more reactive than the vinyl ethers as conventional transfer agents since, by giving up a hydrogen atom, they could yield stabilized allylic radicals. It may be interesting to compare the allyl and vinyl ethers as monomers and comonomers in radical polymerizations.

It is instructive to compare as transfer agents the allyl ethers with allylbenzene (3-phenyl-1-propene) [7] and allyl cyanide (3-cyano-1-propene) [8] which have been investigated by a comparatively new method in which transfer constants are evaluated by considering the end-groups derived from an initiator such as azobisisobutyronitrile (AIBN). The sensitivity required in the end-group analyses can readily be achieved by using AIBN labeled with carbon-14; restrictions on the use of radio-isotopes have made it impracticable to continue the use of ^{14}C-AIBN so that it has been necessary to adopt other procedures for finding the transfer constants for the allyl ethers.

An allyl ether could be incorporated in polymer by a conventional growth reaction:

$$P_n\cdot + CH_2\mathbf{:}CH\cdot CH_2\cdot OR \rightarrow P_n\cdot CH_2\cdot\cdot CH_2\cdot OR \qquad (1)$$

That process might possibly be followed by:

$$P_n\cdot\ CH_2\cdot\dot{C}H\cdot CH_2\cdot OR \rightarrow P_n\cdot CH_2\cdot CH\mathbf{:}CH_2 + \cdot OR \qquad (2)$$

in which case the allyl ether would be functioning as a transfer agent by addition and then fragmentation; there is however, as yet, no evidence to that effect. The action of an allyl ether as a transfer agent is more likely to be that represented thus:

$$P_n\cdot + CH_2\mathbf{:}CH\cdot CH_2\cdot OR \rightarrow P_nH + CH_2\mathbf{:}CH\cdot\dot{C}H\cdot OR \qquad (3)$$

Stabilization of the product radical may cause reinitiation to be inefficient so that the polymerization is retarded and the transfer is described as degradative. Support for a scheme of this type in the case of allyl acetate was provided by the results of experiments involving selectively deuterated allyl acetate [9] and subsequently, by study of the effects of high pressures on the processes of transfer and retardation [10]. Hydrogen-abstraction is not necessarily exclusively according to

Equation 3, and it has been demonstrated experimentally for certain allyl carbonates that abstraction by the *tert*-butoxyl radical occurs significantly at sites other than those suggested by consideration of Equation 3 [4]. Similar conclusions were reached from semi-empirical molecular orbital calculations about the reaction of the hydroxyl radical with allyl carbonates [11].

Another point of interest in connection with the allyl ethers considered here is the possibility that the radical produced in the first stage of transfer according to Equation 4 might dissociate thus:

$$\mathrm{CH_2\!:\!CH{\cdot}\dot{C}H{\cdot}OR} \rightarrow \mathrm{CH_2\!:\!CH{\cdot}CHO + R{\cdot}} \qquad (4)$$

This reaction might be preferred because the carbonyl group is formed. Published information on copolymerizations involving acrolein [12] suggests that, if any of the compound is produced in systems involving allyl ethers, it would subsequently be incorporated to an appreciable extent in polyMMA, poly STY or poly ACN; in most cases, the radical R· would not be so stabilized that it would be noticeably inefficient in reinitiating polymerization.

The present study has centered upon effects of some allyl ethers upon the rates of polymerization of MMA, STY, and ACN using AIBN as initiator at 60°C. Benzene was used as diluent for systems involving MMA or STY and dimethylformamide (DMF) for those in which ACN was used; in all cases, the systems remained homogeneous throughout the reactions. Attention was also paid to the effects of the allyl ethers upon the molecular weights of the polymers. The transfer constants were found from assessments by size exclusion chromatography (SEC) of the molecular weights of the polymers. In the case of allyl phenyl ether, copolymers with MMA and ACN were characterized by consideration of their ^{1}H-NMR spectra; monomer reactivity ratios for the copolymerizations were then calculated.

EXPERIMENTAL

The experimental procedures were essentially those used previously during work involving vinyl ethers [1, 2, 3]. The ethyl and phenyl allyl ethers were obtained from Aldrich and the hydroxyethyl ether from Lancaster Synthesis; the ethers were distilled and their identities and purities were confirmed by GC/MS.

RESULTS AND DISCUSSION

The extent to which allyl phenyl ether was incorporated in polymers of MMA were found by comparing the integrated ^{1}H-NMR signals from "aromatic hydrogens" with those from hydrogens of methoxy groups. The levels of inclusion of the ether in polymers of ACN were found by comparison of the integrated ^{1}H-NMR signals from "aromatic hydrogens" with those from hydrogens of other types in the polymers. It was necessary first to decide whether the allyl phenyl ether had been combined in the polymers or had merely been occluded. Clear evidence that some at least of the ether was chemically incorporated was provided by the ^{13}C-NMR spectra of the polymers. Each of the four distinct carbon sites within the phenyl groups gives rise to a cluster of lines with patterns typical of those observed as a consequence of microstructural variances among the adjacent monomeric units in the polymer chains. If the phenyl signals had been due to occluded material, they would have consisted of four single lines. That the purified polymers contained essentially no occluded allyl phenyl ether was established by the results of test separations.

A sample of pure polyMMA was dissolved in toluene and mixed with allyl phenyl ether, the relative amount of which exceeded those used in the polymerizations leading to the polymers referred to in Table 1. PolyMMA was recovered from the solution by precipitation in methanol, purified by reprecipitation from solution in ethyl acetate and finally dried in vacuum. The ^{1}H-NMR spectrum of the recovered polymer contained no signals which could be attributed to "aromatic hydrogens", showing that the polymer was free from occluded allyl phenyl ether. A similar test involving a mixture of polyACN with allyl phenyl ether in solution in DMF showed again that the procedure for purification of the polymers was entirely satisfactory.

Table 1 refers to polymers of MMA or ACN prepared at 60°C from systems containing allyl phenyl ether; conversions did not exceed 7%. The polymers were purified as in the test separations. Their ^{1}H-NMR spectra contained clear and isolated signals close to 7 ppm (see Figure 1) which must have arisen from phenyl groups belonging to allyl phenyl ether (APE) units incorporated in the polymers. Comparisons of the appropriate spectral areas led to the relative numbers of APE and MMA or ACN units in each of the polymers (see Table 1). There was only slight incorporation of APE in the polymers of MMA so that the quantitative results for those systems are uncertain.

It was impractical to use a similar procedure for assessing the incorporation of APE in polySTY because of the overwhelming influence of the "aromatic hydrogens" in the STY units. A comparison was made however of the ^{1}H-NMR spectrum of "ordinary" polySTY made by radical polymerization at 60°C with the spectrum of the polymer obtained under similar conditions from a system in

Table 1. Copolymers of Methyl Methacrylate (MMA) or Acrylonitrile (ACN) Allyl Phenyl Ether (APE)

	polymer -A	polymer -B	polymer -C	polymer -D	polymer -E	polymer -F	polymer -G
[MMA]/[APE] in feed	1·29	0·86	0·64	0·59	–	–	–
[MMA]/[APE] in copolymer	38·0	31·0	25·5	22·0	–	–	–
[ACN]/[APE] in feed	–	–	–	–	2·50	1·79	1·39
[ACN]/[APE] in copolymer	–	–	–	–	13·0	9·7	7·0

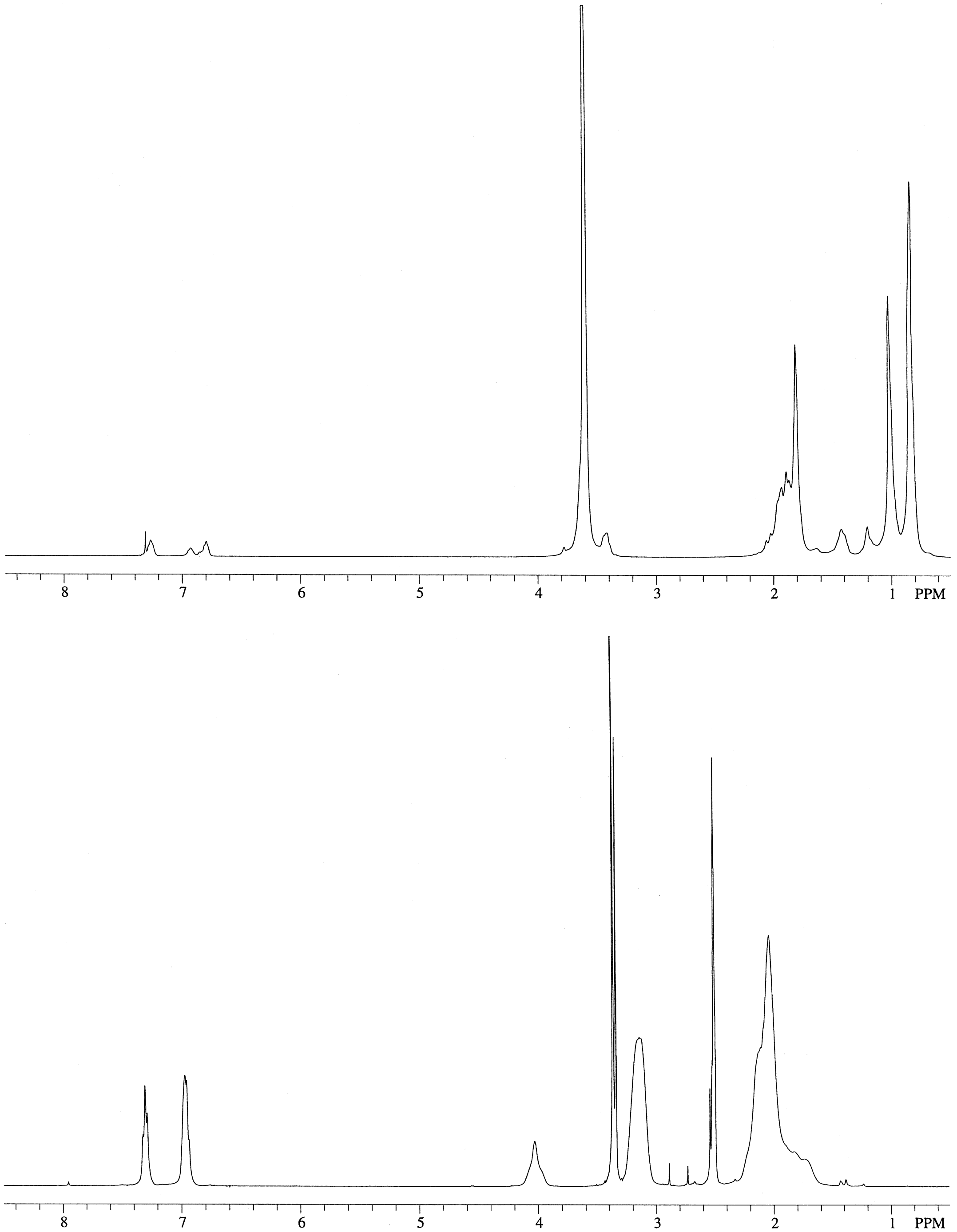

Figure 1. Examples of 400 MHz ^{1}H-NMR spectra of polymers prepared from systems containing allyl phenyl ether. Upper spectrum - poly(methyl methacrylate) in $CDCl_3$; polymer C of Table 1. The sharp signal at 7·4 ppm is due to $CHCl_3$. (Area for signals between 3·3 and 3·4 ppm)/(Area for signals between 6·6 and 7·4 ppm) = 15·5. Lower spectrum - polyacrylonitrile in d_6-dimethylsulphoxide; polymer F of Table 1. Substances of low molecular weight are responsible for the sharp signals:- 2.5 ppm - residual protons in d_6-dimethylsulphoxide; 2·7 and 2·8 ppm - dimethylformamide; 3.4 ppm - contaminant as yet unidentified. (total area for signals in the ranges 1.4-2.4, 3.0-3.3 and 3.9-4.2 ppm)/(area for signals between 6.8 and 7.4 ppm) = 6.8

which [APE]/[STY] was 0.78. Slight difference between the spectra would be expected if there had been appreciable inclusion of APE in the polymer but the spectra were indistinguishable indicating that incorporation of APE in polySTY by copolymerization is negligible.

$\overline{DP}_n$ for polymer-A was found as 705 so that on average there were about 18 APE units in each molecule of that polymer. For polymer-E, $\overline{DP}_n$, was 385 so that the average molecule contained about 40 APE units. These results show that the ether units could not have been confined to sites at the ends of the macromolecules and therefore that some copolymerization had occurred. It was shown that APE does not homopolymerize under conditions like those for the copolymerizations. Benzene containing AIBN and APE at 4.67 x 10^{-2} and 4.26 mol dm^{-3} respectively, kept under anaerobic conditions at 60°C for 50 hours, became slightly discolored but yielded no polymer when added to methanol or hexane.

The Kelen-Tüdos plot [13] (Figure 2) for ACN (monomer-1) with APE leads to $r_1 = 5.7 \pm 1.2$ and $r_2 = 0{\cdot}33 \pm 0{\cdot}08$. For MMA (monomer -1) with APE, the least-squares plot gives a negative value for r_2; the line drawn in Figure 2 seems to be reasonable and leads to $r_1 = 32 \pm 6$ and $r_2 = 0.03 \pm 0.03$. The errors in the derived monomer reactivity ratios can be associated with uncertainties in the integration of the NMR spectra especially for MMA/APE.

The effects of allyl ethers on rates of polymerization (R_p) were studied by dilatometry for the following sets (a), (b), and (c); values of R_{po} refer to polymerizations for which [allyl ether] was zero. For the cases where an allyl ether was present, it replaced part of the diluent, i.e., benzene or DMF as appropriate:

(a) [AIBN] = 1.40×10^{-2} mol dm^{-3}; [MMA] = 2·46 mol dm^{-3}; [allyl ether] up to 2.44 mol dm^{-3}; $R_{po} = 8.93 \times 10^{-5}$ mol dm^{-3} s^{-1}.
(b) [AIBN] = 3.02 x 10^{-2} mol dm^{-3}; [STY] = 3.33 mol dm^{-3}; (allyl ether] up to 3.66 mol dm^{-3}1 R_{po} = 3.73 x 10^{-5} mol dm^{-3} s^{-1}.
(c) [AIBN] = 1.42 x 10^{-2} mol dm^{-3}; [ACN] = 3.97 mol dm^{-3}; [allyl ether] up to 3.66 mol dm^{-3}; R_{po} = 16·60 x 10^{-5} mol dm^{-3} s^{-1}.

In each case, R_p was calculated on the assumption that the relationship between contraction and conversion was unchanged when the nature of the medium was altered by the presence in the system of an allyl ether at a concentration comparable with that of the other monomer. It was assumed that the incorporation of allyl ether in a polymer was small enough to allow the rate of contraction to be converted into the rate of consumption of the main monomer.

Figure 3 shows the effects of the allyl ethers upon the rates of polymerization for MMA, STY, and ACN. Retardation is most noticeable for ACN and least so for STY. For MMA and ACN, allyl hydroxyethyl ether appears to produce comparatively slight effects; the increase in rate for STY could be misleading arising from the assumptions made in calculation of rates of polymerization. It is also possible that partial replacement of the diluent by an allyl ether may have affected the rates of the component reactions in the overall process of polymerization, including the formation of radicals from AIBN.

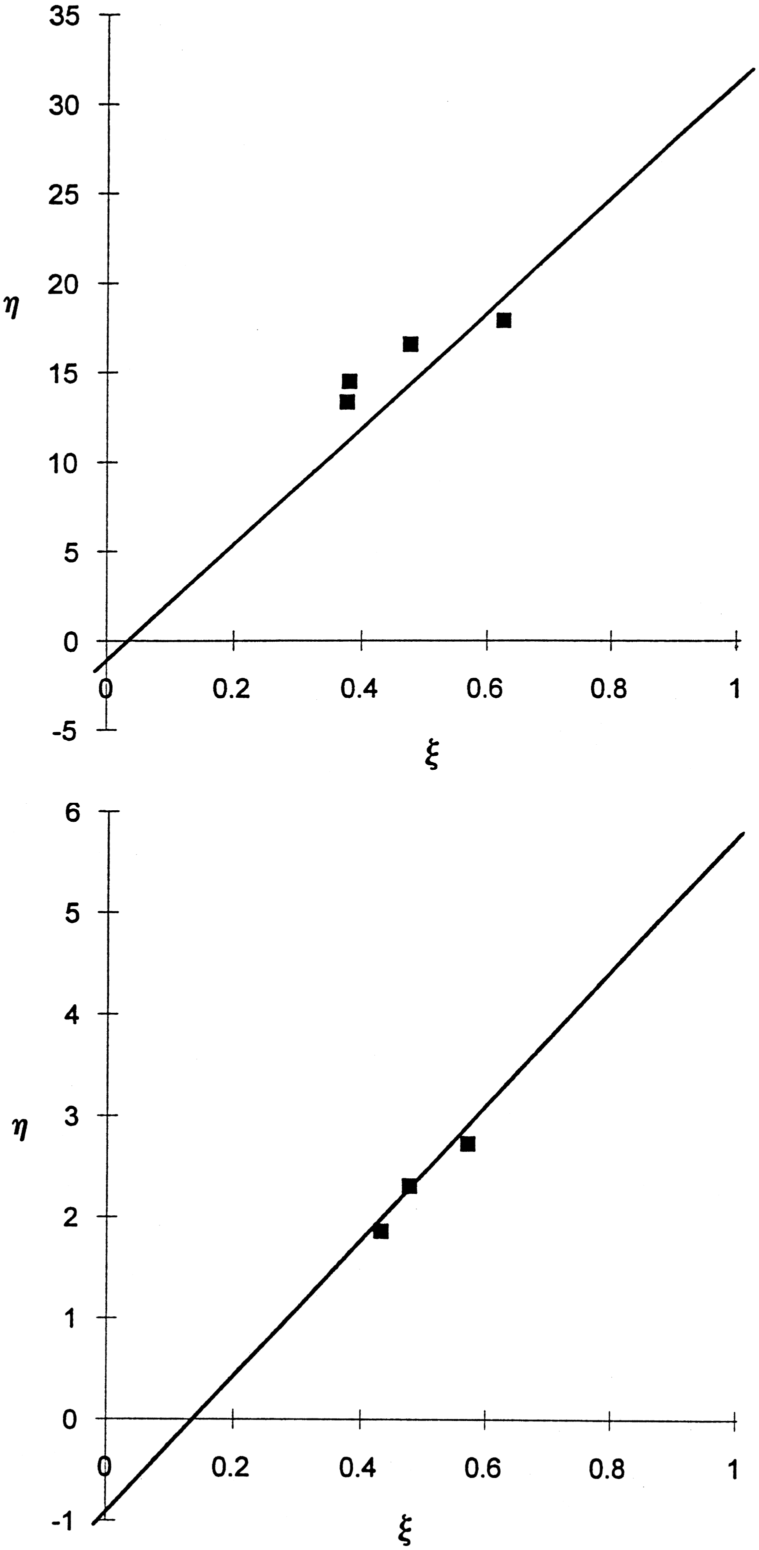

Figure 2. Kelen-Tüdos plots for systems involving allyl phenyl ether. Upper line - methyl methacrylate; lower line - acrylonitrile.

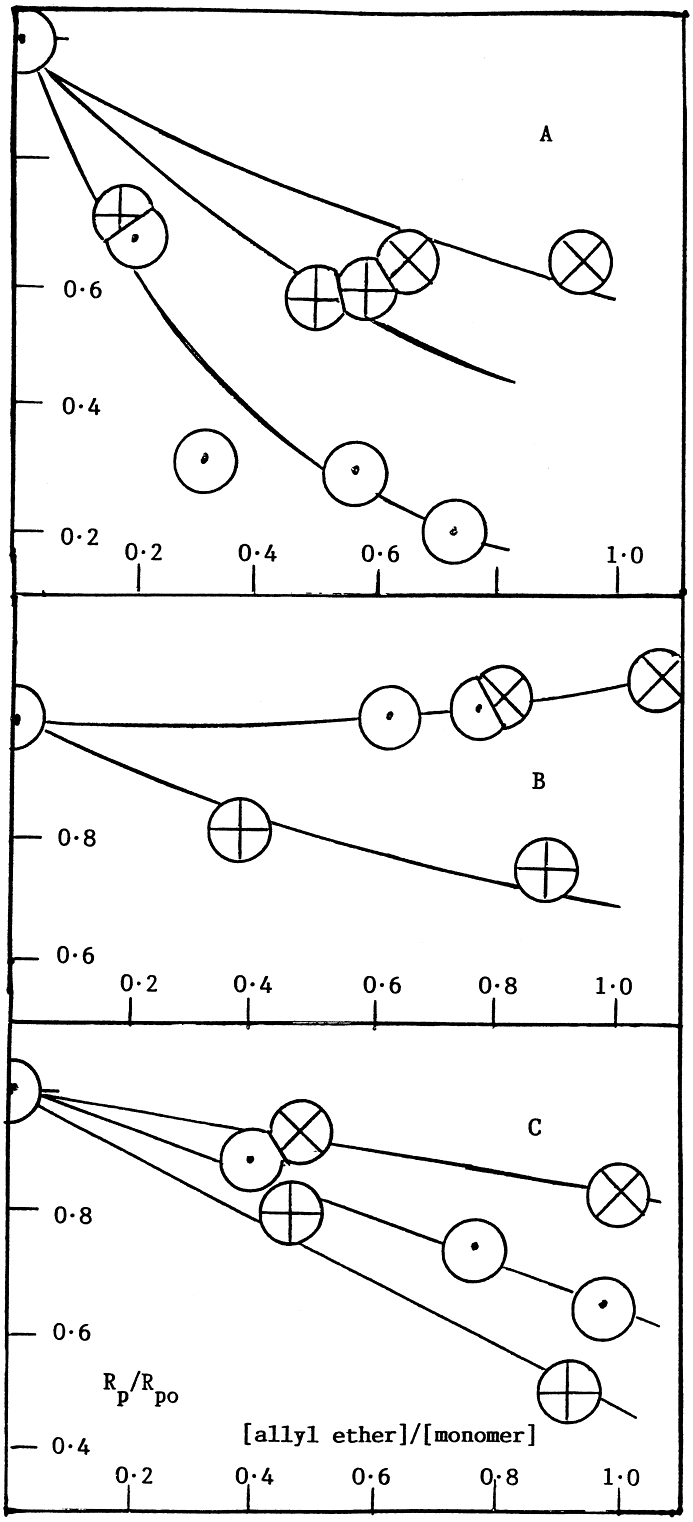

Figure 3. Effects of allyl ethers on rates of radical polymerizations at 60°C. A - acrylonitrile; B - styrene; C - methyl methacrylate. Concentrations of monomers and initiator are given in the text. Allyl 2-hydroxyethyl allyl ether ⊗ ; allyl ethyl ether ⊕ ; allyl phenyl ether ⊙ . Ordinate - (rate of polymerization)/(rate for system without allyl ether); abscissa - [allyl ether]/[monomer].

It was noticed that the allyl ethers appear to be initiators of radical polymerizations at 60°C; the subject will be discussed in detail elsewhere. The hydroxyethyl ether is the most effective of the three allyl ethers as an initiator and its power might be just sufficient to affect appreciably the results; in systems resembling those referred to in Figure 3, it gives rise to rates of polymerization of up to 25% of the appropriate values of R_{po}. It must mean that the rate of initiation, supposedly corresponding to a particular value of [AIBN], increases as [allyl hydroxyethyl ether] is raised so that the retarding effects of the ether must be greater than apparent according to Figure 3.

The molecular weights of most of the polymers derived from the cases referred to in Figure 3 were estimated by SEC and comparisons with standards; they were used for Mayo plots of $1/\overline{DP}_n$ vs. [allyl ether]/[monomer]. Precision is not claimed for the derived transfer constants largely because of the limited numbers of polymers examined but also because of retardation in most of the polymerizations so that the simple treatment is not strictly applicable. The additional initiation, particularly for the hydroxyethyl ether, must make the derived transfer constants a little larger than the true values; the effect would be caused by the enhancement of the rate of initiation by itself bringing down the average molecular weights of the polymer to an extent depending on the concentration of the allyl ether.

Attention must be drawn to the polymers of STY; the rather low molecular weights caused uncertainty in the positioning of the base lines in the chromatograms. The polydispersities of some of the polymers appeared to be in the range 2.6–3.0 even though the polymerizations were run to only low conversions and there seemed to be no kinetic abnormalities. It was concluded that the results for $\overline{DP}_n$ might be unreliable and values of $1/2\ \overline{DP}_w$ were used in the Mayo plots because there is less uncertainty about the precise values of $\overline{DP}_w$ of MMA [14]. It can probably be justified even for the present cases involving STY although combination is normally considerably more important than disproportionation during its polymerization at 60°C so that $\overline{DP}_w/\overline{DP}_n$ is expected to be between 1.5 and 2.0; the occurrence of transfer during the polymerizations involving allyl ethers must have increased the true polydispersities towards 2.0.

The polydispersities of some of the polymers of ACN appeared to be in the region of 2.3 and so values of $1/2\ \overline{DP}_w$ were used for the Mayo plots in these cases also. For each of the polymers of MMA, the polydispersity was between 1.6 and 1.75; these comparatively low values are to be expected because the smallest molecules in the polymers must have been lost during the recovery by precipitation in methanol [15].

Figure 4 shows the Mayo plots. The values of the transfer constants are given in Table 2; errors of up to ± 20% can be expected. The Table also contains results for allylbenzene and allyl cyanide, found from analyses of polymers for end-groups derived from AIBN; there is fair agreement with the values in parentheses, obtained by application of the Mayo treatment to limited data [8].

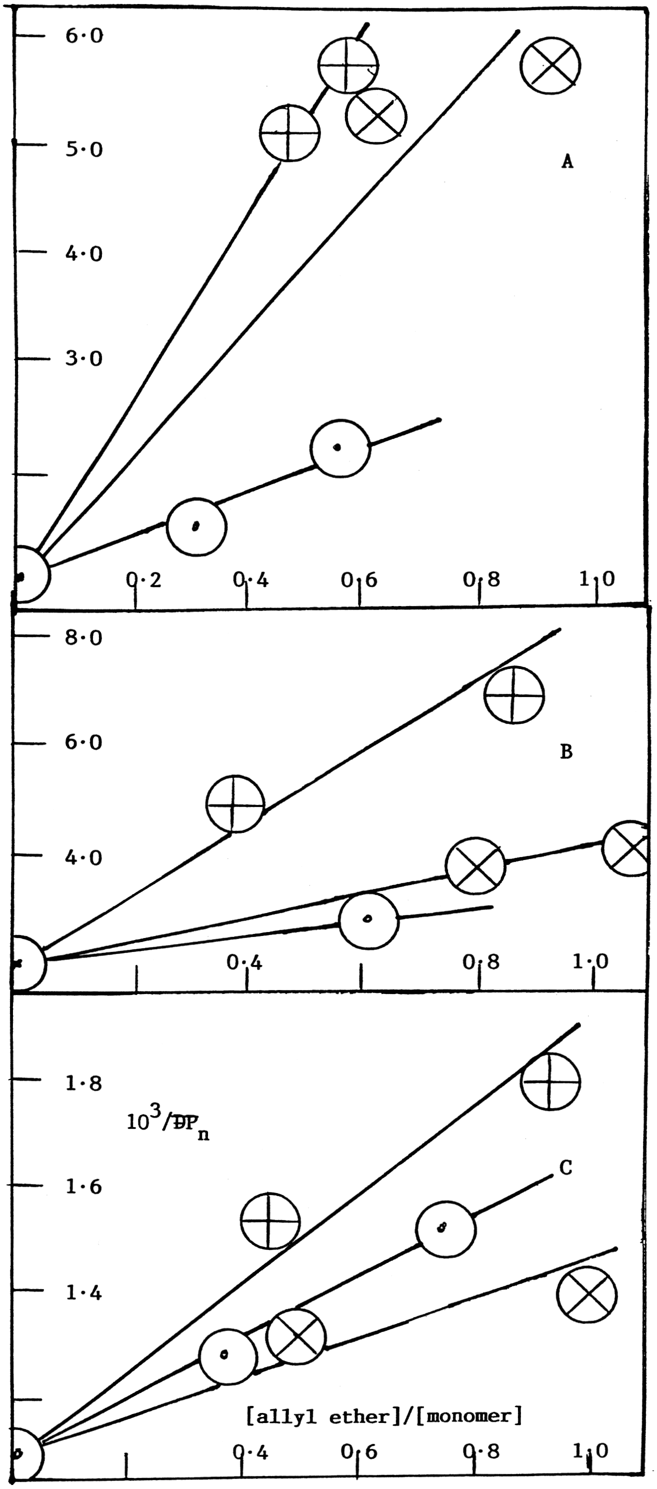

Figure 4. Mayo plots for allyl ethers with acrylonitrile (A), styrene (B), and methyl methacrylate (C). Allyl 2-hydroxyethyl allyl ether ⊗ ; allyl ethyl ether ⊕ ; allyl phenyl ether ⊙ . <u>Ordinate</u> - 10^3/DPnfor polymer; <u>abscissa</u> - [allyl ether]/[monomer].

Table 2. Transfer Constants for Allyl Ethers and Other Allyl Compounds (All Values Have Been Multiplied by 10^3)

	Allyl Ether				
Monomer	Phenyl	Ethyl	2-Hydroxyethyl	Allyl benzene[a]	Allyl cyanide[b]
MMA	0·3	0·6	0·3	5·0	0·6(0·5)
STY	0·4	2·9	0·9	5·0	3·0(4·0)
ACN	2·0	8·2	6·0	–	–

[a] See Ref. 7.
[b] See Ref. 8.

The reactivities of various transfer agents towards a particular polymer radical can be compared directly by considering the values of the appropriate transfer constants. On this basis, results given in Table 2 indicate that, for both MMA and STY, allylbenzene is much more reactive than the allyl ethers and that allyl cyanide resembles the ethers in efficacy as a transfer agent. Allylbenzene is much stronger as a retarder than the ethers or allyl cyanide thus, for MMA with AIBN, R_p/R_{po} is 0·80 if [allyl benzene]/[MMA] is 0·12; at that ratio of concentrations, the allyl ethers cause R_p/R_{po} to be about 0·95 (see Figure 3) and retardation by allyl cyanide is only slight [7, 8].

Generally, there appears to be a correlation between the influences of related retarding additives upon R_p for a particular monomer under specified conditions and their effects upon the molecular weights of the resulting polymers, as indicated by the magnitude of the transfer constants. If transfer occurs readily, the resulting radical is expected to be stabilized to some extent and therefore, to have limited reactivity towards the monomer so that reinitiation is rather inefficient and the overall polymerization is retarded. Moad and Solomon [16] have expressed the view that this so-called thermodynamic control is not as important as once assumed, but it appears that stability of the product radical really is a factor of importance in transfer processes, involving some allyl compounds. The radical $CH_2\mathbf{:}CH{\cdot}\dot{C}H{\cdot}Ph$ is likely to be formed from allylbenzene and, because of the presence of the phenyl group, delocalization of the unpaired electron is probably much more significant than for radicals of general formula $CH_2\mathbf{:}CH{\cdot}\dot{C}H{\cdot}OR$ formed from allyl ethers. This view is consistent with the finding that, as a transfer agent with MMA or STY, allylbenzene is more reactive than the allyl ethers or allyl cyanide and that it is also a stronger retarder.

The information in Table 2 indicates that, for each of the three monomers, allyl ethyl ether is clearly the most reactive of the three ethers as a transfer agent and that the phenyl ether may be the least reactive. These conclusions are not in line with the effects of the ethers upon rates of polymerization; Figure 3 shows that the phenyl ether is the strongest retarder for ACN and that the hydroxyethyl ether is the weakest for both ACN and MMA. These findings can be only tentative in view of initiation apparently by the allyl ethers themselves as already referred to.

For comparisons of the reactivities of a particular transfer agent in processes such as (3) during the polymerizations of several monomers, it is necessary to know not only the various transfer constants (k_f/k_p) but also the values of k_p for the growth reactions. There are considerable differences between the values of k_p for common monomers.

The transfer constants for ACN with the allyl ethers are several times the corresponding quantities of MMA and STY. The values of k_p at 60°C for ACN, MMA, and STY can be taken as 2460, 830, and 340 mol^{-1} dm^3 s^{-1}, respectively [17]; it is clear therefore, that k_f for the reaction of a polyACN radical with an allyl ether is substantially larger than k_f for the relevant reaction involving either a polyMMA or a polySTY radical. The results in Table 2 suggest that the transfer constants for STY with the allyl ethers are a little larger than those for MMA; k_p for STY is smaller than k_p for MMA so that the values of k_f for the two monomers are not very different.

The Kelen-Tüdos plot for ACN (monomer-1) with allyl phenyl ether (APE) indicated that r_2 might be 0.33, a value suggesting that a polymer radical with an APE unit at its reactive end might capture another molecule of the ether to give a short sequence of adjacent APE units. This conclusion is not necessarily at variance with the finding that APE appears not to undergo homopolymerization at 60°C with AIBN as initiator; it is possible that oligomers of the ether might be formed but would not be recovered as solids insoluble in methanol or n.hexane. It is necessary also to consider the possibility that a complex ACN/APE is formed and is involved in the copolymerization; complexes between electron-rich and electron-deficient monomers are thought to engage in some copolymerizations [18], such effects might arise in systems involving allyl ethers. Comparisons of the ^{1}H- and ^{13}C-NMR spectra for solutions in d_6-dimethylsulphoxide of ACN , APE and their equimolar mixture gave no indication whatsoever of the existence of a complex.

For MMA (monomer-1) with APE, r_1 is found to be 32; there is great uncertainty about the precise value of r_2, but clearly it is close to zero. The situation is therefore, very different from that for ACN with APE; there is at present no reasonable explanation for the large difference between the values of r_2 for the two systems. As explained already, it is possible only to say that involvement of APE in copolymerization with STY must be very slight.

Various vinyl ethers increased the rate of the radical polymerization of ACN, as monitored either dilatometrically or gravimetrically [3]. The effect was not due to initiation caused by the ether; it was attributed to decrease in the rate of termination in the polymerizations, caused by the reaction media being poor solvents for the polymers, and it outweighed any retardation due to degradative transfer. Similar effects were not found for the allyl ethers with ACN and rates of polymerization were reduced to greater extents than for STY or MMA. It can only be supposed that the incorporation of the allyl ether in polyACN was sufficient to modify the solubility of the polymers, leading to significant improvement in the quality of the reaction media as solvents for the polymers.

Reports on the involvement of allyl ethers in polymerizations are not numerous. The diallyl ether was considered in a study of the reactivities in radical systems of allylic monomers covering a wide range including allyl alcohol and allyl amine [19]. It was concluded that the polymerizability and the importance of degradative transfer for a compound $CH_2\mathbf{:}CH{\cdot}CH_2{\cdot}X$ depend on the polar characteristics of the group -X. The substances examined here were all ethers (-X = -0·R) so that they must be very similar in respect of effects of the group -X on the allyl group. Polymers derived from isopropenyl ethers, formed by isomerization of allyl ethers, have attracted considerable attention but the polymerizations are cationic not radical [20].

CONCLUSION

The allyl ethers resemble the vinyl ethers in showing little tendency to engage in radical polymerization and copolymerization with styrene or methyl methacrylate but allyl phenyl ether enters fairly readily into copolymerization with acrylonitrile. The allyl ethers act as degradative transfer agents; the retardation is more significant with acrylonitrile than with styrene or methyl methacrylate, but it is less than when allylbenzene is used. The transfer constants for the ethyl, 2-hydroxyethyl and phenyl allyl ethers with acrylonitrile are several times larger than the corresponding quantities for styrene and methyl methacrylate.

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