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FURTHER STUDY OF ALLYL ETHERS AND RELATED COMPOUNDS AS TRANSFER AGENTS IN RADICAL POLYMERIZATIONS

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ABSTRACT

Allyl glycidyl ether (AGE), allyl 1,1,2,3,3,3-hexafluoropropyl ether (AFE), allyl 2-naphthyl ether (ANE), 2-vinyl-1,3-dioxolane (2VD) and allyl alcohol (AA) have been examined as transfer agents in the radical polymerization of methyl methacrylate (MMA) at 60°C; the transfer constants are 1.1×10^{-3} , 0.1×10^{-3} , 0.2×10^{-3} , 1.1×10^{-3} and 0.6×10^{-3} , respectively. AFE and AA barely affect the rate of polymerization: AGE, ANE, and 2VD act as weak retarders. There is no direct correlation between effectiveness as a transfer agent and the extent of retardation for these additives. For copolymerization with MMA (monomer-1), the monomer reactivity ratios r_1 are 42 ± 5 and 32 ± 5 for AGE and ANE, respectively; for both cases, r_2 is very close to zero; 2VD engages in copolymerization with MMA to a negligible extent. Experiments involving styrene or acrylonitrile gave results consistent with those obtained using MMA.

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

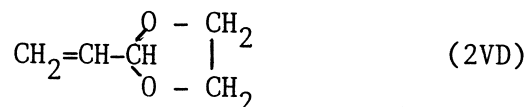
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INTRODUCTION

A report has been given [1] on the effects of certain allyl ethers on radical polymerizations of methyl methacrylate (MMA) and styrene (STY) in benzene and acrylonitrile (ACN) in dimethylformamide (DMF) at 60°C using azoisobutyronitrile (AIBN) as initiator. It followed a similar study of vinyl ethers [2]. The allyl ethers considered were the ethyl, phenyl and 2-hydroxyethyl compounds (AEE, APE, and AHE, respectively); attention was paid to their roles as transfer agents and retarders and as possible co-monomers. It has also been shown [3] that at least some of the allyl ethers appear to act as feeble initiators of radical polymerizations; it was concluded however that the effects are probably due to peroxides present in the ethers as a result of auto-oxidation.

The work on the effects of unsaturated additives upon the radical polymerization of MMA has been extended to 2-vinyl-1,3-dioxolane (2VD) a compound



which can properly be regarded as closely related to the allyl ethers of general formula $\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{R}$. It has already been demonstrated [3] that at 60°C 2VD seems to be a source of radicals initiating polymerizations and explanations have been offered for the differences between its effects with MMA, STY and ACN. Consideration is also given here to allyl alcohol (AA) and three further allyl ethers, viz. allyl glycidyl ether (AGE), allyl 1,1,2,3,3,3-hexafluoropropyl ether (AFE) and allyl 2-naphthyl ether (ANE) as possible transfer agents and retarders. The possibilities of copolymerization of AGE, ANE, or 2VD with MMA have been examined.

EXPERIMENTAL

Allyl 2-naphthyl ether was prepared by the alkylation of 2-naphthol with allyl bromide; it was finally purified by column chromatography on silica gel. The allyl ethers, 2VD and AA were commercial products (Aldrich) and were purified by distillation; GC/MS was used to confirm their identities and purities. Other materials were purified by standard procedures.

Polymerizations were performed at 60°C under anaerobic conditions, most of them with AIBN as initiator but a few with benzoyl peroxide (BPO); they were monitored by dilatometry and conversions were less than 5%. Benzene was the diluent used with MMA and STY but DMF was used with ACN; in all cases, about 25% of the system consisted of monomer. Polymers were recovered by precipitation in methanol and reprecipitated from solutions in toluene or DMF; some polymers from MMA/ANE systems were finally purified by precipitation from

solutions in ethyl acetate in order to eliminate the possibility of occlusion of aromatic solvent.

Molecular weights of polyMMA and polySTY samples were found by Size Exclusion Chromatography using standard polymers for reference and treating all polymers as homopolymers of MMA or STY as appropriate. $^1\text{H-NMR}$ spectra were recorded for solutions in CDCl_3 using a JEOL GSX-400 spectrometer.

RESULTS AND DISCUSSION

2VD acts as a feeble retarder for the polymerizations of MMA and STY at 60°C (see Figure 1); lines show the greater retardation for MMA by the allyl ethers previously studied [1]. 2VD is a transfer agent in the polymerizations; Mayo plots are given in Figures 2 and 3. The values of k_t/k_p for 2VD/MMA from the three pairs of points are 1.0×10^{-3} , 1.1×10^{-3} and 1.2×10^{-3} ; both plots for 2VD/STY give k_t/k_p as 0.6×10^{-3} .

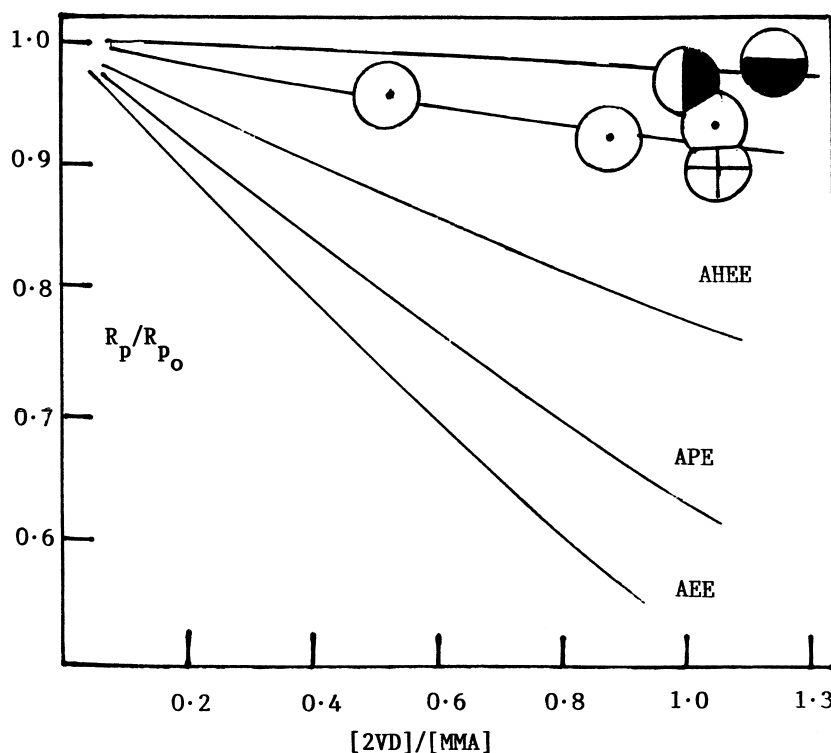


Figure 1. Effects of 2VD on rate of polymerization (R_p). R_{p_0} = rate in absence of 2VD for appropriate values of [monomer] and [initiator]. \odot MMA/AIBN; \oplus MMA/BPO; \bullet STY/AIBN; \bullet STY/BPO.

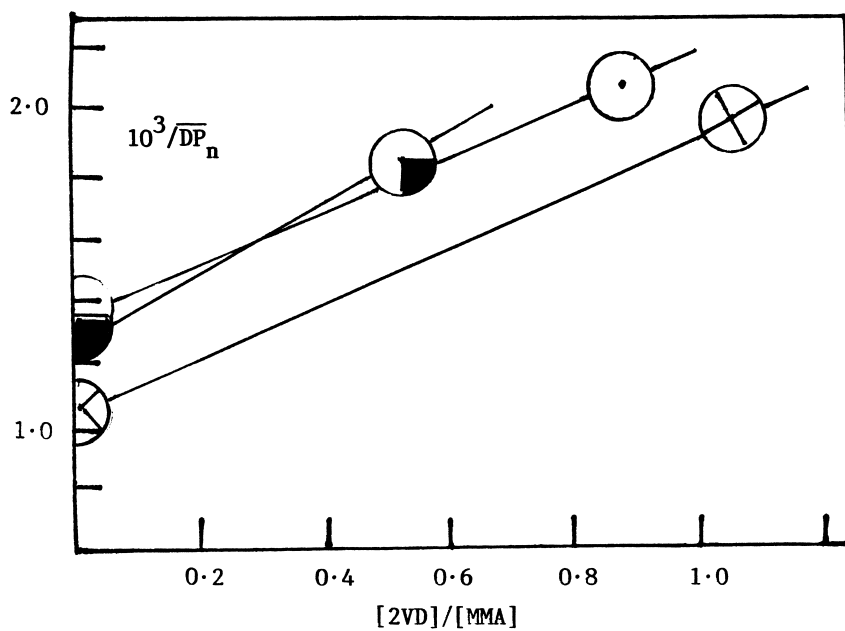


Figure 2. Mayo plots for 2D with MMA.

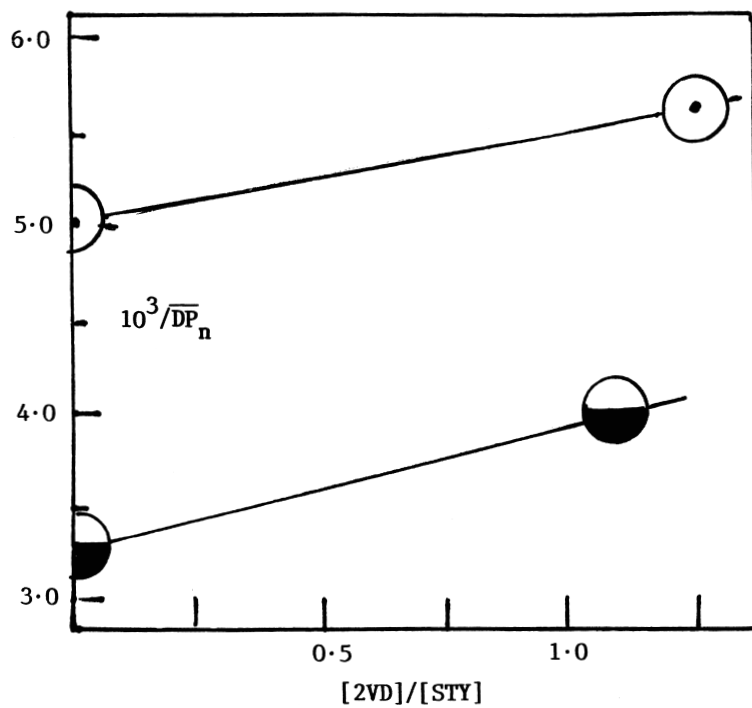
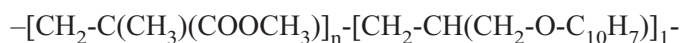


Figure 3. Mayo plots for 2D with STY.

Figure 4 shows the effects of additives on R_p for the systems AGE/MMA, ANE/MMA, AGE/ACN and AA/ACN. R_p for MMA was almost unaffected when $[AA]/[MMA]$ was 1.30 or when $[AFE]/[MMA]$ was 0.66. ANE retarded the polymerization of MMA only slightly but its effect for ACN was much greater and R_p was reduced almost to zero when $[ANE]/[ACN]$ was 0.25.

Mayo plots for MMA with the additives are shown in Figure 5; reasonable values for the transfer constants seem to be 0.1×10^{-3} (AFE), 0.2×10^{-3} (ANE), 0.6×10^{-3} (AA) and 1.1×10^{-3} (AGE); for each of these quantities there may be uncertainties of about $\pm 15\%$.

An example of a $^1\text{H-NMR}$ spectrum of a polymer is shown in Figure 6; it refers to a sample of polyMMA made in the presence of ANE. The integrated signals between 7 and 8 ppm (corresponding to "aromatic" hydrogens) are compared with the integral of the signal at 3.6 ppm (corresponding to hydrogens attached to carbons adjacent to oxygen). The sharp signal at 7.3 ppm is due to CHCl_3 present in CDCl_3 at about 1 part in 1000; it corresponds to less than 10% of the spectral area attributed to "aromatic" hydrogens and appropriate allowances have been made in calculations. If the polymer is represented as



$$\frac{\text{hydrogens on C adjacent to O}}{\text{"aromatic" hydrogens}} = (3n+2)/7$$

and n can be evaluated from information deduced from the $^1\text{H-NMR}$ spectrum.

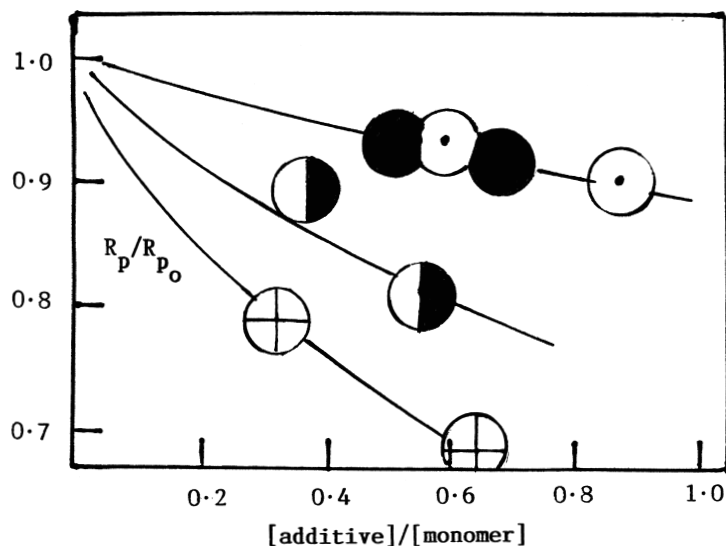


Figure 4. Effects of additives on rate of polymerization initiated by AIBN. R_{p_0} as defined for Figure 1. ○ AGE/MMA; ● ANE/MMA; ◐ AGE/ACN; ⊕ AA/ACN.

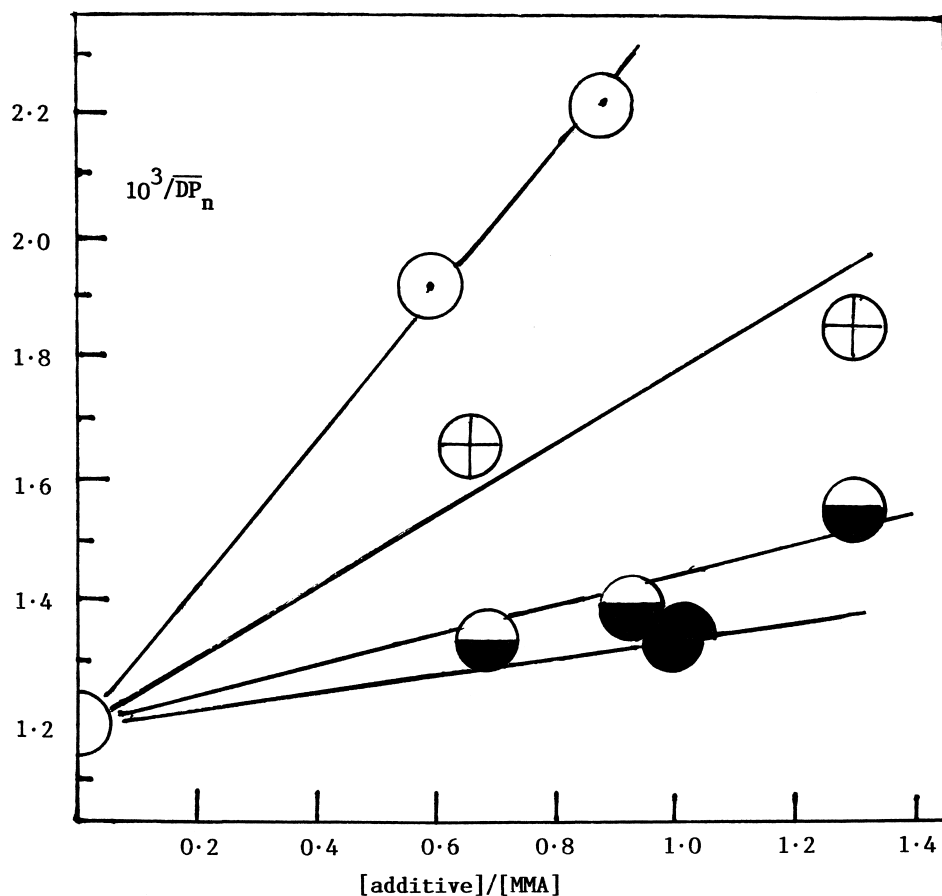
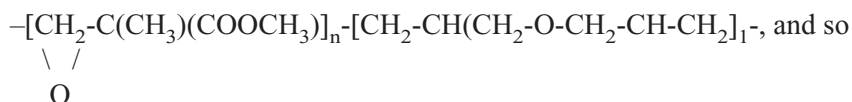


Figure 5. Mayo plots for additived with MMA. ● AGE; ⊕ AA; ◐ ANE; ● AFE.

For copolymers of MMA/AGC, the spectral area covered by the signals at 3.6 ppm is compared with that covered by signals between 0.8 and 2.2 ppm arising from other "aliphatic" hydrogens. The polymer can be represented as:



$$\frac{\text{hydrogens on C adjacent to O}}{\text{other aliphatic hydrogens}} = \frac{3n + 7}{5n + 3}$$

and n can be found from the spectral areas. The results for the systems ANE/MMA Kelen-Tüdös method [4] gives values of 42 ± 5 and 32 ± 5 for the monomer reactivity ratio r_1 for AGE/MMA and ANE/MMA, respectively; for both systems, r_2 is very close to zero.

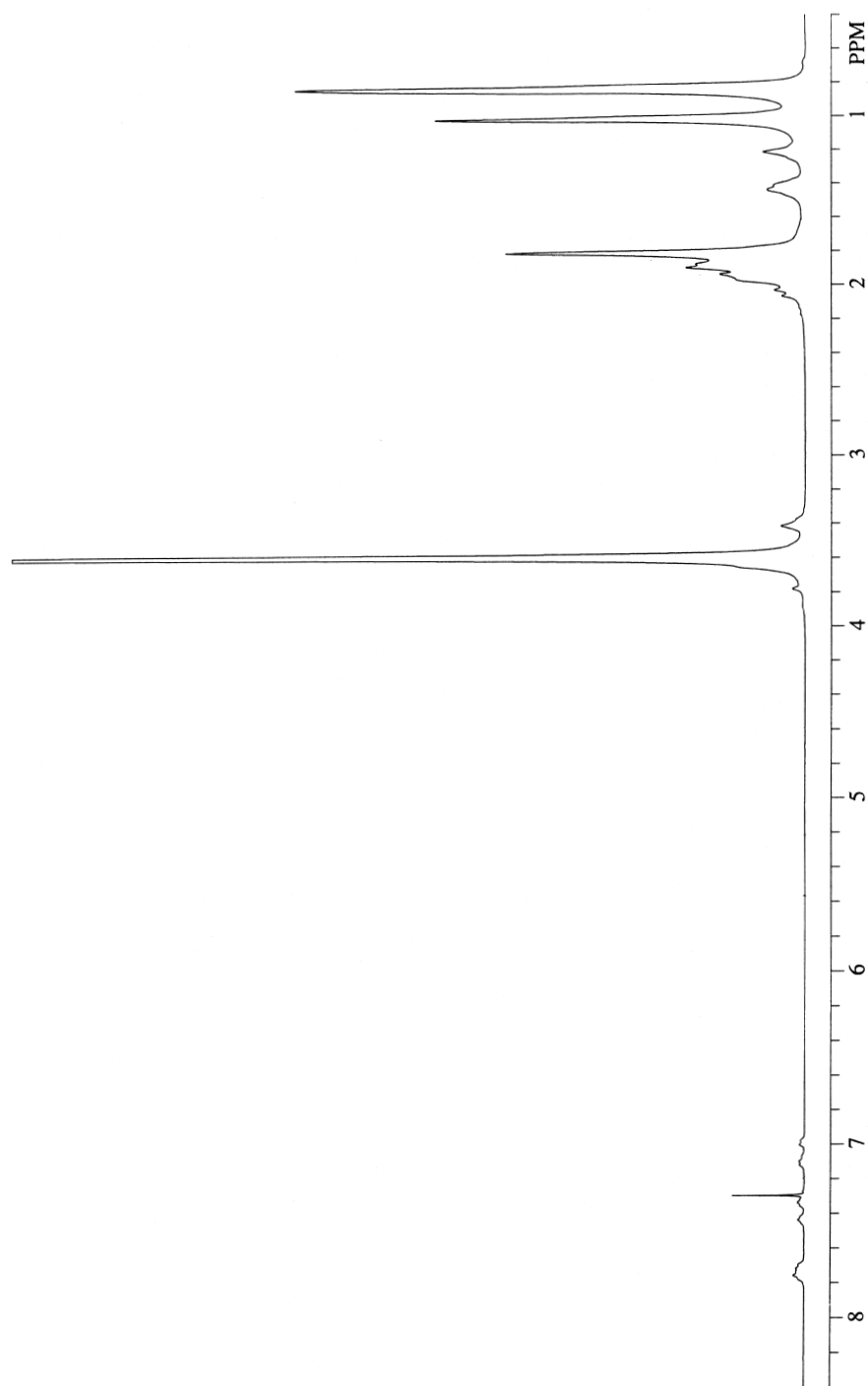


Figure 6. 400 MHz ¹H-NMR spectrum of polyMMA prepared in benzene solution in the presence of ANE at 60°C using AIBN as initiator; polymer finally precipitated in methanol from solution in ethyl acetate. [MMA] = 2.54 mol dm⁻³, [ANE] = 2.21 mol dm⁻³, [AIBN] = 1.22 × 10⁻² mol dm⁻³; \overline{M}_n of polymer = 73,000.

No evidence was found for incorporation by copolymerization of 2VD in polyMMA. If it had occurred to any appreciable extent, it would have been detectable in a comparison of the spectral areas corresponding to 3.6 and 0.8-2.2 ppm.

The transfer constants for MMA with AEE, APE and AHE are 0.6×10^{-3} , 0.3×10^{-3} and 0.3×10^{-3} , respectively [1]; of these ethers, AEE causes the greatest retardation. These findings are in line with the view that, for a series of related compounds, the substance having the largest transfer constant is likely to give rise to the most stable and least reactive product radical; re-initiation is therefore least efficient for that substance and its retarding effects are greatest. Similar relationships have been quite widely accepted for reactions of other types also e.g. growth processes in copolymerizations [5] although Moad and Solomon [6] have suggested that the importance of this "thermodynamic control" may have been exaggerated.

The results for 2VD certainly do not conform to the pattern for the three allyl ethers previously studied; the transfer constants with MMA and STY are comparatively large at 1.1×10^{-3} and 0.6×10^{-3} , respectively and yet its retarding effects are slight (see Figure 1). It is now suggested that not all the radicals formed from 2VD during transfer are produced by abstraction of hydrogen from carbon-2 of the dioxolane ring and that many result from removal of hydrogen from carbon-4 or -5; the resulting radicals would not be appreciably stabilized and so would be quite reactive. A similar point has been made previously when it was shown that, in systems resembling those considered here, abstraction of hydrogen is not solely from the site leading to an allylic radical and may occur to significant extents from other carbon atoms also [7]. In the case of 2VD, abstraction from carbon-4 or -5 might be favored due to the availability of four hydrogen atoms and also because of the proximity of the oxygen atoms of the dioxolane ring.

The transfer constant for the system AGE/MMA is 1.1×10^{-3} i.e., as large as that for 2VD/MMA; the two additives are also very similar in their effects on R_p (compare Figures 1 and 4). For reasons such as those discussed in connection with 2VD, it is thought that abstractions of hydrogen atoms from the glycidyl group are important perhaps because each of its three carbon atoms is adjacent to an oxygen atom.

AA is moderately effective as a transfer agent for MMA ($k_t/k_p = 0.6 \times 10^{-3}$), but it has no appreciable influence on R_p for that monomer, suggesting that production of an allylic radical is of little significance; the alternative of abstraction of hydrogen from the -OH groups is most unlikely. It is conceivable that AA functions by a mechanism not involving abstraction of hydrogen from its molecule (vide infra).

The effects of ANE on the polymerization of MMA are less than those of APE; the transfer constant is 0.2×10^{-3} instead of 0.3×10^{-3} and the retardation is noticeably less than that caused by APE (compare Figures 1 and 4). AFE produces little retardation and with MMA k_t/k_p is only 0.1×10^{-3} . Clearly, formation of the allylic radicals cannot occur readily and the fluoro-propyl group contains

only one hydrogen atom so that reaction at that part of the molecule is rather unlikely. The strongly electronegative fluorine atoms may also exert effects.

The high values of the monomer reactivity ratio r_1 for the copolymerization of MMA with AGE or ANE show that the reaction of a polyMMA radical with MMA monomer is greatly favored over its reaction with an allyl ether. The very low values of r_2 show that a polymer radical having an allyl ether unit at its reactive end shows little tendency to react with another molecule of an allyl ether; there is therefore, only a very small chance of two allyl ether units at adjacent sites in a polymer chain. The values of r_1 for APE/MMA and ANE/MMA are hardly distinguishable, but that for AGE/MMA is probably a little larger. The polymers referred to in Table 1 had number-average molecular weights in the region of 50,000 to 100,000 so that, for each of them, the average molecule contained between about eight and 30 units derived from an allyl ether; these numbers are far too high for any suggestion that the allyl ethers are incorporated only as a result of transfer reactions. If for some reason there were a need to prepare a polymer having a few ether linkages in pendant groups distributed along the chains, it could be met by using allyl ethers at moderate concentrations as comonomers.

No data are available on transfer constants for ACN with the additives now considered, but the previous work with allyl ethers [1] showed that the transfer constants for ACN are several times larger than the corresponding quantities for STY and MMA and that retardation is generally more evident for the systems involving ACN. In the case of ANE, R_p for ACN is reduced almost to zero for quite small concentrations of the additive although R_p for MMA is not greatly affected. Retardation for the systems AGE/ACN and AA/ACN is prominent and much greater than when MMA is used as the monomer. It may be that the polyACN radical differs from the polyMMA radical in its tendency to abstract hydrogen from the sites of various types in the molecules of the additives. It is necessary also to consider that ACN may be appreciably less reactive than MMA towards the radicals formed by abstraction of hydrogen so that re-initiation becomes less efficient and retardation more evident.

It has been pointed out [1] that allyl ethers might possibly act as transfer agents by the "addition-fragmentation" mechanism. The process would be represented thus

Table 1. Copolymers of Methyl Methacrylate with Allyl Ethers

	Feed	Copolymer
[MMA]/[AGE]	1.14	51
[MMA]/[AGE]	1.68	68
[MMA]/[ANE]	1.15	40
[MMA]/[ANE]	1.45	50
[MMA]/[ANE]	1.96	60



although a reasonable scheme of that type cannot be constructed for 2VD. Generally, the product radical $\cdot OR$ would not be stabilized so that re-initiation would be efficient and the whole process of transfer would not lead to retardation. It is possible that an occurrence of transfer of this type would be the basis of an alternative explanation for the finding that some of the additives, e.g. AGE and AA, are quite active as transfer agents in the polymerizations of MMA and STY but do not cause appreciable reduction in R_p ; in the case of AA, the product radical would be $\cdot OH$ which reacts readily with all common monomers. There is as yet no positive evidence for "addition-fragmentation" in the systems under consideration and indeed it might be regarded as improbable in view of the retarding effects of AA upon the polymerization of ACN (see Figure 4).

CONCLUSION

For allyl ethers and related compounds, there is no direct correlation between effectiveness as a transfer agent in the radical polymerization of methyl methacrylate and power as a retarder of the polymerization. If "thermodynamic control" of the transfer process were dominant, the more reactive transfer agents should yield more stable and, therefore less reactive radicals so that retardation becomes more evident; it is clear that this is not so. It is concluded that abstraction of hydrogen from the molecules of certain of these additives occurs to an appreciable extent in a manner not producing an allylic radical. The glycidyl and 2-naphthyl allyl ethers are incorporated in poly(methyl methacrylate) to a very limited extent by copolymerization.

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