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EFFECTS OF VINYL ETHERS UPON RADICAL POLYMERIZATIONS

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ABSTRACT

Various vinyl ethers have been examined as additives during radical polymerizations initiated by azobisisobutyronitrile at 60°C; the monomers were methyl methacrylate (MMA), styrene (STY) and acrylonitrile (AN). For MMA and STY, the vinyl ethers were incorporated to only small extents but they caused reductions in rate of polymerization and chain length of the resulting polymer; the effects can be attributed to the low reactivities in growth reactions of radicals to which a vinyl ether unit was last added. Copolymerization of the vinyl ethers with AN was more evident but, in many cases, it was accompanied by increased rate of consumption of AN and increased chain length of the polymer. These changes can be explained in terms of a physical effect

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which can be likened to that believed to be responsible for the gel effect. It is considered that polymer radicals are rather tightly coiled in an indifferent solvent so that the normal bimolecular termination is impeded.

INTRODUCTION

Copolymers of methyl methacrylate (MMA) or styrene (STY) with certain vinyl ethers (VEs) have been prepared by radical polymerization using ^{13}C-enriched samples of azobisisobutyronitrile (AIBN) or benzoyl peroxide as initiator; the end-groups derived from the initiator have been examined by ^{13}C-NMR [1]. It has been deduced that the VEs are rather unreactive towards the radical $Me_2C(CN)\cdot$ derived from AIBN, in agreement with results obtained by Heberger and Fischer [2] using a completely different procedure; on the other hand, the VEs react quite readily with the radical Ph-CO-O· formed by dissociation of the peroxide [1].

Copolymerizations of various VEs with MMA have been studied using ^{1}H-NMR to analyze the resulting copolymers [3]. Regarding the VE as monomer-2, the monomer reactivity ratio r_2 is in each case close to zero meaning that a polymer radical to which a VE unit was last added has little tendency to capture immediately another molecule of VE. For compounds $CH_2{=}CH{-}O{-}R$ in which R– is a comparatively small and compact alkyl group such as t-butyl, the monomer reactivity ratio r_1 is in the region of 4·0; when R– is a sizeable alkyl group such as n-dodecyl or n-octadecyl, r_1 is about 12. These values of r_1 indicate that the VEs do not compete effectively with MMA for reaction with the polyMMA radical. This conclusion is consistent with the finding that these ethers have low reactivities towards the carbon-centred radical $Me_2C(CN)\cdot$ and also with the results obtained by a new (Revised Patterns) approach to the prediction of monomer reactivity ratios, taking the radical $Me_2C(CN)\cdot$ as a model for the polymethacrylonitrile radical [4, 5].

Some copolymers of STY (monomer-1) with VEs were analyzed; deficiencies in the experimental procedure meant that values of r_1 could not be found precisely but it was evident that they are appreciably greater than those for the corresponding systems involving MMA. This finding is in accord with the predictions of the new treatment already referred to [4, 5].

Information is now given about rates of polymerizations and molecular weights of polymers recovered from copolymerizations at 60°C of MMA or STY with certain VEs in benzene solution using AIBN as initiator. Consideration is given also to systems involving acrylonitrile (AN) with VEs using N,N-dimethylformamide (DMF) as diluent and AIBN as initiator at 60°C. In this connection, published data on the monomer reactivity ratios are used.

One of the points of interest in the VEs as comonomers is the possibility that they might act as transfer agents by addition followed by fragmentation according to the scheme:

$$P_n\text{–}CH_2\text{–}CH(OR)\cdot \rightarrow P_n\text{–}CH_2\text{–}CHO \quad + \quad R\cdot$$

Such a process might be favored due to the formation of the carbonyl group. Considerable attention is being paid to transfer processes of this type [6] and an attempt is made now to assess their possible significance during the polymerizations of MMA, STY or AN in the presence of certain VEs. It is recognized that the ethers being considered are likely to be much less effective as addition/fragmentation transfer agents than specially selected unsaturated ethers such as CH_2=CPh–O–CH_2Ph. Nevertheless, points arising from the present studies may be of importance quite generally.

EXPERIMENTAL

Most of the experimental procedures have been described already [1, 3]. Monomeric AN was treated with alumina, distilled in nitrogen and stored at –20°C over molecular sieves. Polymerizations were performed under anaerobic conditions and were monitored by dilatometry. Polymers were recovered by precipitation in methanol containing a small amount of calcium chloride to assist in coagulation of the precipitate.

Size exclusion chromatography of copolymers rich in AN and homopolymers of AN was performed with equipment consisting of a Waters 510 pump, Rheodyne 7125 injector fitted with 200 µl loop, PL gel mixed “B” columns (3 × 30 cm with guard column) and a Hewlett-Packard 1047A RI detector. The columns were thermostatted at 70°C. Polymers were dissolved in DMF to give concentrations of 0·25% w/v and spiked with aniline as a flow-rate marker 200 µl Samples of solutions were injected and eluted with DMF containing 0·1% w/v ammonium acetate. Data were collected and analyzed using a

Polymer Laboratories data station equipped with "CALIBER" software. The system was calibrated with poly(ethylene oxide)/poly(ethylene glycol) standards.

RESULTS AND DISCUSSION

Table 1 provides information on systems in which the principal monomer was either MMA or STY and VEs were used as comonomers. There was no inhibition in the polymerizations and steady rates of reaction were found. The VEs retarded the polymerizations with reduction in the molecular weight of the resulting polymers. The effects were not large and it was not possible to draw firm conclusions about any differences between the magnitudes of the influences of the various VEs. The quoted rates of polymerization were found by dilatometry, treating the reactions as homopolymerizations of the principal monomer; similarly the values of $\overline{\mathrm{DP}}_n$ for the copolymers were based on the assumption that they could be regarded as behaving in SEC as if they were homopolymers.

TABLE 1. Polymerizations Involving Methyl Methacrylate or Styrene

Expt. No.	[monomer]/ (mol dm^{-3})	[vinyl ether]/ (mol dm^{-3})	10^5 (rate of polymn.)/ (mol dm^{-3} s^{-1})	$\overline{\mathrm{DP}}_n$ of polymer
1	2·15 MMA	0	6·74	880
2	2·15 MMA	TBVE; 0·87	5·93	867
3	3·15 MMA	0	10·12	1010
4	3·15 MMA	NPVE; 1·79	7·98	878
5	3·15 MMA	DDVE; 0·53	9·82	940
6	3·15 MMA	DDVE; 1·47	8·20	–
7	3·01 STY	0	3·24	150
8	3·01 STY	NPVE; 0·92	3·28	140
9	3·01 STY	NPVE; 1·54	2·87	140

NPVE, TBVE and DDVE – n-propyl, t-butyl and n-dodecyl vinyl ether respectively.

10^2[AIBN] in mol dm^{-3} – 1·00 (expts. 1 & 2), 1·10 (expts. 3-6), 3·40 (expts. 7-9).

These treatments are unlikely to have caused serious errors since the incorporation of VE was small in each case; copolymer-4 was the richest in the ether and [MMA]/[VE] in it was close to 8·0. There is a clear tendency for the effects on rate of polymerization and $\overline{DP}_n$ to be less for STY than for MMA; this difference is consistent with the fact that incorporation of the VEs in polySTY is even less than that in polyMMA.

The retardation and reduction in molecular weight are likely to be directly associated with a radical of low reactivity produced by the interaction of a growing centre with a molecule of the VE. This radical might be P_n–CH_2–CH(OR)· formed in a growth reaction or a radical produced from the VE in a transfer process of either a conventional type or one involving addition/fragmentation. The following argument shows that transfer reactions are probably not important processes for the VEs considered here.

Of the experiments in which MMA was monomer-1, expt.-5 corresponded to the highest value of [MMA]/[VE]; DDVE was used and so r_1 was about 12, i.e., greater than for the cases of MMA with NPVE or TBVE. Application of the usual copolymer composition equation, taking r_2 as zero, shows that [MMA]/[VE] in the copolymer was about 72. $\overline{DP}_n$ for the polymer was 940 sothat the average macromolecule must have contained about 13 DDVE units. There must have been larger numbers of VE units in the average molecule of the other copolymers based on MMA since the VE contents were higher than for copolymer-5 and the values of $\overline{DP}_n$ were similar. If a transfer agent functions in a simple manner, there cannot be more than one of its molecules incorporated in the average polymer molecule; this requirement is certainly not met for the cases of NPVE, TBVE and DDVE with MMA. It is evident therefore, that, if these VEs engage in addition/fragmentation during polymerization with MMA, they do so inefficiently; if fragmentation ever occurs, it can do so after only quite a small fraction of the additions.

Some of the publications on addition/fragmentation for specially selected agents seem to have paid little attention to the possibility that on occasions there can be addition without ensuing fragmentation. It is reasonable to suppose that the likelihood of fragmentation is greatest when the concentration of the main monomer is low so that there is comparatively little chance of the process being suppressed by the addition of another unit of the principal monomer. There is a formal resemblance with a system in which a monomer having quite a low ceiling temperature for its homopolymerization can enter into copolymerization with a monomer for which the ceiling temperature is noticeably higher. These considerations lead to the view that, for addition/fragmentation, the transfer constant would depend upon the concentration of the monomer; the constant would be greater when [monomer] is low.

Copolymerizations of AN with VEs differ in important aspects from those involving MMA or STY with the unsaturated ethers. The VEs copolymerize with AN (monomer-1) much more readily than with the other monomers, published values of r_1 lying between about 0·7 and 1·0 and those of r_2 being close to zero [7]; the only exception appears to be vinyl phenyl ether for which r_1 and r_2 have been given as 2·5 and 0·23 respectively. The **u**, **v** and π parameters for typical VEs, reported previously [5], are entirely consistent with these observations. Using the mean values for VEs containing short alkyl groups, the values of r_1 and r_2 predicted for copolymerizations in which monomer-1 is STY, MMA or AN are respectively 47 and 0, 14·5 and 0, and 0·85 and 0·05. For the copolymerization of AN (monomer-1) with vinyl phenyl ether, the Revised Patterns Scheme predicts that r_1 is 2·15 and r_2 is 0·23. In subsequent calculations, r_1 and r_2 for copolymerizations of AN with the VEs now under consideration are taken as 0·8 and zero respectively. Another special feature which may affect the reactions is the limited solubility of polyAN and copolymers rich in AN; DMF was needed as diluent for the reactions in order to maintain homogeneity of the systems. The products were insoluble in monomeric AN and in the VEs themselves; in some cases, the proportions of monomeric AN, DMF and VE in the mixtures might have been such that the liquids could not have been good solvents for the copolymers. This point was confirmed by the observation that systems rather rich in VE became opalescent during polymerization.

Many copolymerizations were performed using AN and AIBN with a VE using DMF as diluent, the proportions being such that the systems appeared to remain homogeneous throughout the polymerizations up to about 7% conversion of the AN. The reactions were monitored by dilatometry and they showed no apparent abnormalities. Invariably however the rate of contraction for a copolymerization was greater than that for the corresponding homopolymerization in which the VE had been replaced by additional DMF; for example, the rates of contraction for a homopolymerization of AN at 2·07 mol dm^{-3} and copolymerizations using the same concentrations of AN and AIBN but with DDVE at 0·35 or 0·88 mol dm^{-3} were in the ratios 1:1·3:1·9 and generally similar effects were found when using other VEs.

Figure 1 clearly illustrates the contrast between the retarding effects of VEs on the rates of contraction for polymerizing systems involving MMA and

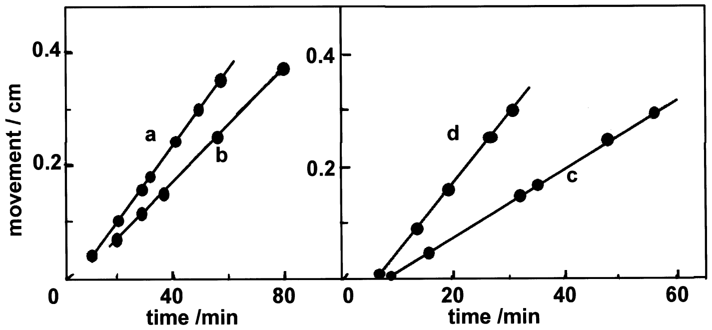

Figure 1. Examples of dilatometric plots showing the movement with time of the meniscus in the capillary and demonstrating the effects of VEs upon the polymerizations of MMA and AN at 60°C. (a) MMA, expt.-3 in Table 1; dilatometer-A; (b) MMA with NPVE, expt.-4 in Table 1; dilatometer-A; (c) [AN] = 2·07 mol dm^{-3}; [AIBN] = 1·52 x 10^{-2} mol dm^{-3}; dilatometer-B; (d) AN] = 2·07 mol dm^{-3}; [AIBN] = 1·48 x 10^{-2} mol dm^{-3}; [DDVE] = 0·88 mol dm^{-3}; dilatometer-B.

the accelerating effects for cases in which AN was used. It should not be supposed however that the faster contraction for AN containing a VE necessarily indicates that the copolymerization was more rapid than the homopolymerization. Allowance might be needed for the appreciable incorporation of VE in the copolymer; for the cases cited in the preceding paragraph, the values of [AN]/[DDVE] in the copolymers are calculated as approximately 5·7 and 2·9 respectively. More significant information on rates of incorporation of AN in copolymers with VEs was obtained from gravimetric measurements; the treatment of the results is illustrated with examples.

A copolymerization was performed with AN and DDVE at 3·97 and 1·01 mol dm^{-3}, respectively, AIBN at 1·50 × 10^{-2} mol dm^{-3} and DMF as diluent; the total volume of the system was 2·3 ml. After 2100 s at 60°C, 0·115 g of polymer had been produced. [AN]/[DDVE] in the copolymer is calculated as 4·1 so that the formula weight of the average monomeric unit was 84 and the overall rate of polymerization must have been 0·115/(84 × 2100 × 2·3 x 10^{-3}) i.e., 28·3 x 10^{-5} mol dm^{-3} s^{-1} and the rate of incorporation of AN is given by (28·3 × 10^{-5})4·1/5·1 i.e. 22·8 × 10^{-5} mol dm^{-3} s^{-1}. In a similar experiment involving TBVE at 1·99 mol dm^{-3} instead of DDVE, 0·095 g of polymer were formed in 1500 s [AN]/[TBVE] in the copolymer is calculated as 2·6 so that the formula weight of the average monomeric unit was 66. The overall rate of polymerization is calculated as 41·7 × 10^{-5} mol dm^{-3} s^{-1} and the rate of consumption of AN as 30·1 × 10^{-5} mol dm^{-3} s^{-1}.

In a matching experiment without a VE present, AN was found to polymerize at the rate of $14{\cdot}0 \times 10^{-5}$ mol dm^{-3} s^{-1}; an almost identical value was obtained by dilatometry. The rate of incorporation of AN during the "blank" polymerization is considerably less than those in the two reactions involving a VE. Quite substantial alterations to the selected values of r_1 and r_2 do not affect the general trends in the results.

It is concluded that the presence of a VE in a polymerizing system may cause a notable increase in the rate at which AN is incorporated in polymer when the reaction mixture contains only a limited amount of DMF and is therefore an indifferent solvent for the copolymer being produced. The enhancement of the rate of incorporation of AN is, as expected, less marked when [VE] is reduced and [AN] is unchanged. Under these circumstances, the proportion of DMF in the system is increased and the mixture becomes a better solvent for the copolymer; this change of itself may affect the rate. The effect of increasing the proportion of DMF in the system from 45% by volume, as in the cases considered in the preceding paragraph, to 55% is shown by the following example.

For AN at $4{\cdot}05$ mol dm^{-3} in DMF with AIBN at $1{\cdot}40 \times 10^{-2}$ mol dm^{-3}, the rate of polymerization was determined gravimetrically as $17{\cdot}2 \times 10^{-5}$ mol dm^{-3} s^{-1}. In a corresponding copolymerization involving DDVE at $0{\cdot}64$ mol dm^{-3}, the overall rate of polymerization was found as $21{\cdot}2 \times 10^{-5}$ mol dm^{-3} s^{-1} and the rate of consumption of AN as $18{\cdot}1 \times 10^{-5}$ mol dm^{-3} s^{-1} i.e., only slightly and perhaps not significantly greater than when no VE was present.

VEs caused retardation rather than acceleration of the polymerizations of MMA and STY (see Table 1). The quoted rates of polymerization were obtained dilatometrically but the trends were fully confirmed by subsequent gravimetric measurements both for cases in which benzene was the diluent and for others in which DMF was used. The products of the polymerizations were readily soluble in the mixtures of principal monomer, VE and diluent.

It is suggested that, in those cases where the presence of a VE caused a marked increase in the rate of polymerization of AN, the effect can be attributed to comparatively tight coiling of the growing radicals in a medium which is not a good solvent for the polymer; the radical sites may therefore be shielded to some extent. The monomer molecules are mobile and so it is supposed that growth reactions are little affected; however termination may be impeded because normally it requires the meeting of the reactive ends of two macroradicals. Polymerizations in media which are very poor solvents for the polymer being produced are accompanied by special effects; a notable example is the bulk polymerization of AN. It was shown some time ago that in such cases the polymer radicals are trapped in the precipitated polymer and both growth and termination reactions may be impeded [8]. This situation probably arises when comparatively large amounts of VE are used and the systems become opalescent as reaction proceeds, as already reported.

The explanation proposed for the present results resembles that generally accepted to account for the gel effect in certain radical polymerizations viz. that the rate of termination is reduced because of a physical effect. If it is valid, the presence of VE in the polymerizing system would be expected to cause the molecular weight of the polymer to be higher than that of polymer produced in a similar system not containing VE; there is some evidence that this is so. A system in which [AN] was 2·7 mol dm^{-3} in DMF yielded polymer for which $\overline{\mathrm{DP}}_n$ was 530 by SEC. In a similar reaction, part of the diluent was replaced by DDVE so that [DDVE] was 0·88 mol dm^{-3} corresponding to about 23% by volume; the resulting polymer was subjected to SEC using the same calibration as for the homopolymer of AN and $\overline{\mathrm{DP}}_n$ was found to be 1320. The result must be regarded as approximate because of the uncertainty about the procedure particularly as the content of DDVE in the polymer was quite high, [AN]/[DDVE] being about 2·9 as stated already; it is however unlikely that the derived value of $\overline{\mathrm{DP}}_n$ would have been higher than the true by a factor as large as about 2·5. It is concluded therefore that the results are consistent with the view that effect of the VE on the rate of incorporation of AN can be attributed to reduction in the rate of termination.

The idea of restricted termination during copolymerizations of AN with VEs might be tested by considering systems consisting of AIBN, AN and DMF with, instead of a VE, a comparatively small amount of a substance which is a non-solvent for polyAN and does not participate in a chemical sense in the polymerization; for this purpose, anisole was selected. It was first shown that anisole has almost no effect on the polymerization of MMA at 60°C. For the polymerization at 60°C of AN at 3·97 mol dm^{-3} with AIBN at $1{\cdot}80 \times 10^{-2}$ mol dm^{-3}, replacement of some of the DMF by anisole so that [anisole] became 1·59 mol dm^{-3} (corresponding to about 18% by volume) caused the rate of polymerization to increase by a factor of 1·2; the comparatively small increase in rate coupled with the fact that some polymer was precipitated during the reaction means that the result cannot be regarded as conclusive. It appears that the copolymers of

AN and VEs are somewhat more soluble than the homopolymer of AN so that the problem of precipitation is encountered only when rather high concentrations of VE are used.

The comments already made concerning inefficiency as transfer agents of the VEs considered here during polymerizations of MMA and STY are applicable with even more force for the polymerization of AN. The monomer reactivity ratios for copolymerizations with VEs are such that, even for quite modest concentrations of VE, the number of VE units incorporated in a typical macromolecule is considerably greater than unity.

CONCLUSION

The radical polymerizations of MMA and STY in benzene are retarded by vinyl ethers such as the n-propyl, t-butyl and n-dodecyl compounds; the chain lengths of the resulting copolymers are less than those of the corresponding homopolymers. The results are consistent with the belief that low reactivity in growth reactions is possessed by a polymer radical to which a vinyl ether unit was last added. Quite different effects may be dominant when the vinyl ethers are used with AN in DMF. The ethers can cause increases in the rate of incorporation of AN in polymer and in the molecular chain length. The changes are attributed to a physical effect. Replacement of some of the DMF by a vinyl ether reduces the solvent power of the medium so that, although polymer radicals remain in solution, they become fairly tightly coiled. There is a formal resemblance with systems in which the gel effect operates; termination is impeded while growth reactions are largely unaffected so that the rate of polymerization and also the chain length of the resulting polymer are increased.

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