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End Groups of Poly(methyl methacrylate-*co*-styrene) Prepared with *tert*-Butoxy, Methyl, and/or Phenyl Radical Initiation: Effects of Solvent, Monomer Composition, and Conversion

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ABSTRACT: The relative reactivities of *tert*-butoxy, methyl, and phenyl radicals toward styrene, methyl methacrylate, and several solvents (acetone, butan-2-one, toluene, and benzene) have been established by means of competition experiments. These experiments demonstrate that when a source of *tert*-butoxy radicals is employed as the initiator for copolymerization and toluene or butan-2-one is used as the solvent, a majority of end groups may be solvent derived. This is a consequence of the *tert*-butoxy radicals' high propensity for hydrogen abstraction. Even with benzene as solvent, there is a significant proportion of solvent attack and resultant phenyl radical initiation. A second major influence of the medium is on the extent to which *tert*-butoxy radicals either undergo β-scission or react by addition or abstraction. Finally, with each of the three radicals (t-BuO$^\bullet$, Me$^\bullet$, and Ph$^\bullet$), there is a small, yet significant, solvent effect on the relative reactivity of styrene and methyl methacrylate. To assess the variation in the distribution of the initiator-derived end groups with conversion the rate data obtained from the competition experiments have been used as the basis for computer simulations of the copolymerization of methyl methacrylate and styrene.

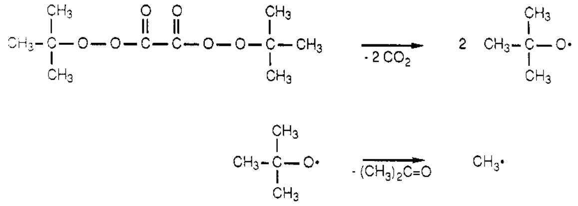
Introduction

Numerous tables of relative rate constants for the reactions of radicals with monomers and other substrates exist in the literature.[1] However, relatively little effort has been devoted to one of the subjects often quoted as the justification for accumulating such information in the first place, namely, the extrapolation from such rate data to a description of the end groups of a polymer or copolymer prepared with free radical initiation. One of the major impediments to using the existing data in this way is that many of the rate constants will be dependent on the specific reaction conditions (solvent, temperature, etc.). Furthermore, aside from the possibility of the reaction medium modifying radical reactivity, many solvents have reactivities approaching those of the monomers, and in specific cases much of the initiation of polymer chains may involve solvent derived radicals.[2]

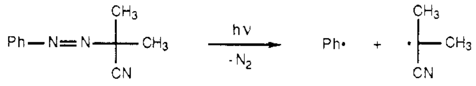
The effects of solvent on free radical reactivity are generally small. There is, however, substantial literature on solvent effects on the relative rates of *tert*-butoxy radical reactions.[1-5] Moreover, recent work carried out in these laboratories has established that for the reaction of *tert*-butoxy radicals with methyl methacrylate (MMA), the relative yield of products from double-bond addition and H-atom abstraction is solvent dependent.[2] It is, therefore, reasonable to question whether, in copolymerization, the selectivity of *tert*-butoxy radical for a given monomer might be dependent on the reaction medium. The influence of solvent on the reactions of methyl and phenyl radicals with monomers has not previously been the subject of systematic investigation.

In this paper we begin to address the above-mentioned problems by reporting on the reactions of *tert*-butoxy, methyl, and phenyl radicals with styrene and MMA as a function of solvent and monomer composition.[6] We then use this data to describe the distribution of end groups in poly(MMA-*co*-styrene) formed with *tert*-butoxy radical initiation. Four solvents were chosen for study, benzene and acetone (often used in fundamental studies of radical reactions) and toluene and butan-2-one (which see widespread industrial application). The reactions have been studied by using the radical trapping technique demonstrated in previous work.[1,7-9]

Scheme I



Scheme II



Results

The competition experiments were carried out at 60 °C either in bulk or with acetone, butan-2-one (MEK), benzene, or toluene (10% v/v) as cosolvent and with 1,1,3,3-tetramethylisoindolin-2-yloxy[10] (0.011–0.05 M) as the trapping agent. Di-*tert*-butyl peroxalate (0.005 M) was used as the source of *tert*-butoxy and methyl radicals (Scheme I). Initially phenyl radicals were generated by thermal decomposition of benzoyl peroxide. However, the long half-life of benzoyl peroxide at 60 °C and the complication of products derived from benzoyloxy radical reactions[8,9] prompted us to examine other methods of generation. Photolysis of 2-(phenylazo)-2-cyanopropane, which has an absorption maximum (at 360 nm) in a window of the nitroxide spectrum, was found to be a clean source of phenyl radicals (Scheme II). While only a small fraction of phenyl radicals are trapped directly as **6c** (see Table VII), the concurrently formed 2-cyanoprop-2-yl radicals are efficiently scavenged by the nitroxide. The alkoxyamine **6i** serves as a useful internal standard since its yield equates with the total yield of phenyl radical products. The distribution of phenyl radical-derived products showed no dependence on the radical source.

The concentration of nitroxide employed was such as to prevent any of the radicals (**1–4r**), the 2-cyanoprop-2-yl radical **8i**, or other radicals formed from the reactions of *tert*-butoxy or phenyl radicals with solvent (acetone, MEK, or toluene) (**8d–h**) undergoing propagation reactions to a significant extent. (For compounds **1–4** the suffix r has been used to designate the radical precursors.)

The identification of products was made on the basis of a HPLC retention time comparison (spiking) with reference materials available from previous work.[1,6-9] The relative rate constants for the reactions undergone by *tert*-butoxy, methyl, and phenyl radicals during the co-

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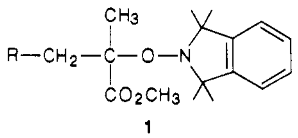

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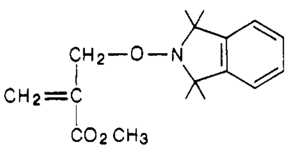

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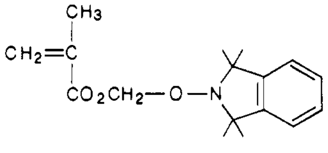

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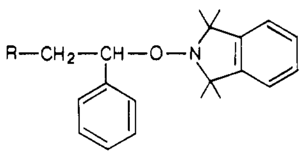
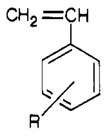
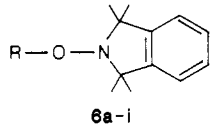


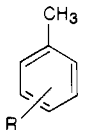
4a–**i**



5a–**i**



6a–**i**



7a–**i**

$R^\bullet$

8a–**i**

- **a**, R = $(CH_3)_3C{-}O{-}$
- **b**, R = $CH_3{-}$
- **c**, R = Ph-
- **d**, R = $CH_3C({=}O)CH_2{-}$
- **e**, R = $CH_3C({=}O)CH_2CH_2{-}$
- **f**, R = $CH_3C({=}O)CH(CH_3){-}$
- **g**, R = $CH_3CH_2C({=}O)CH_2{-}$
- **h**, R = $PhCH_2{-}$
- **i**, R = $(CH_3)_2(CN)C{-}$

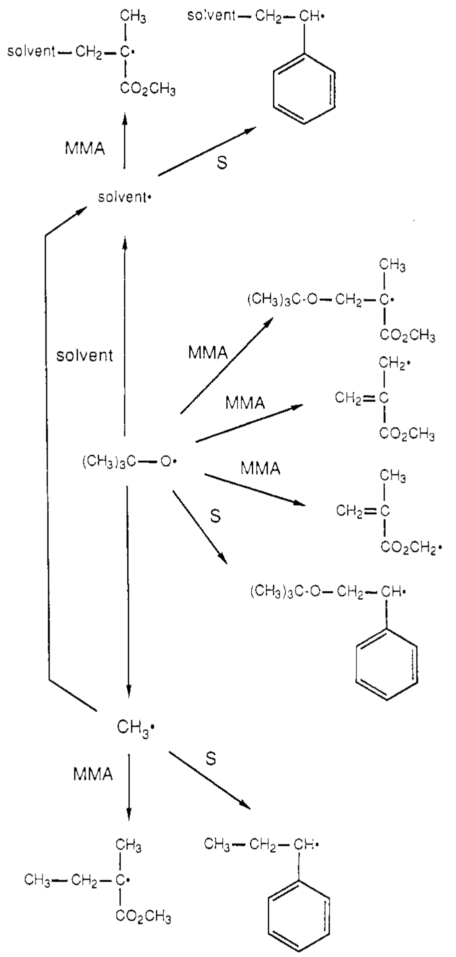
polymerization of styrene and MMA in the four solvents are presented in Table I (refer Scheme III). The relative reactivities shown are based upon the relative amounts of the alkoxyamine adducts that were determined by quantitative HPLC (see Tables II–VII). It is noteworthy that, for the reactions carried out in 90% solvent, no variation in the relative reactivities with monomer ratio was observed.

It was noted in the course of this work and previous studies on the reactions of radicals with methacrylate monomers that the MMA-derived alkoxyamines 1 are unstable if heated for prolonged periods at 60 °C. This arises since the formation of 1 are reversible.[11] Therefore, if sufficiently long reaction times are employed, the reactions of the radicals **1r** with nitroxide by disproportionation (the ratio of combination to disproportionation is >0.99) or with monomer (i.e. oligomer formation) may become significant. To assess the influence of this side reaction on our data, we have monitored the rates of disappearance of these materials 1 at 60 °C in 5:1 (v/v) MMA–styrene both in the presence and absence of added nitroxide (0.01 M). The results of these experiments are summarized in Table VIII. The styrene-derived alkoxyamines 4 were recovered unchanged after being subjected to similar treatment. On the basis of this evidence (and a good material balance for the reported products) it is concluded that for the reaction times employed in our studies, this problem can be neglected.

Discussion

A. Monomer Relative Reactivity—Comparison with Previous Work. The relative reactivity of *tert*-butoxy radicals toward monomers has been studied previously by Encina et al.,[12] who determined the volatile products produced during the photolysis of di-*tert*-butyl peroxide in monomer/cyclohexane/benzene mixtures and indicated that the relative reactivity of the double bond of styrene with respect to that of MMA at 20 °C was 1:0.167.

Scheme III



Sato and Otsu[13] studied *tert*-butoxy radical reactivity by EPR employing a spin trapping method. They reported that the relative reactivity of the double bonds of styrene and MMA at 25 °C was 1:0.058 (abstraction from xylene used as reference reaction). The approximately threefold discrepancy between the latter and our value of 1:0.189 (benzene, 60 °C; see Table I) cannot be readily explained. In view of the findings of Encina et al.[12] (see above), it seems unlikely that temperature should be responsible for an effect of this magnitude and the origin of discrepancy probably lies with the complexities inherent in using the spin-trapping method for quantitative work.[14,15]

Our finding that methyl radicals are less reactive toward styrene than toward MMA (see Table I) is in accord with the results of Szwarc et al.[16] who obtained a relative reactivity of 1:1.81 in isooctane at 65 °C.

Five different groups (see below) have reported data on the reaction of phenyl radicals with styrene and MMA and all found styrene to be less reactive than MMA. Bevington and Ito[17] compared the reactivities of phenyl radicals (generated thermally from benzoyl peroxide) toward several monomers with their tendency to abstract hydrogen from *N*,*N*-dimethylformamide in benzene at 60 °C. Styrene was found to be less reactive than MMA (relative reactivity 1:1.79).[17] Pryor and Fiske[18] referenced the reactivity of phenyl radicals (from triphenylmethylazobenzene) toward a variety of substrates to the radicals ability to abstract hydrogen from heptanethiol and came up with a similar relative reactivity (1:1.69 at 60 °C). Levin et al.[19] also used triphenylmethylazobenzene as a phenyl radical source but used abstraction of chlorine from carbon

Table I
Relative Rate Constants[a,b] for *tert*-Butoxy and Methyl Radical Reactions at 60 °C as a Function of Solvent (Refer to Scheme III)

reaction	solvent: acetone	butan-2-one	benzene	toluene
t-BuO•				
add MMA	0.174 ± 0.001	0.176 ± 0.005	0.187 ± 0.003	0.182 ± 0.003
abs MMA[c]	0.11	0.11	0.095	0.091
abs solv	0.025	0.17	0.00095	0.19
scission	0.23	0.20	0.11	0.08
Me•				
add MMA	1.92 ± 0.08	2.10 ± 0.06	1.85 ± 0.05	*d*
react solv[e]	0.005	0.011	0.00029[f]	0.0032
Ph•				
sub sty	<0.01	<0.01	<0.01	<0.01
add MMA	1.22	1.14	1.00	1.03
abs solv	0.006	0.028	*g*	0.010
sub solv			0.006	0.003
Ph• (10 °C)[h]				
add MMA		1.66		1.08

[a] Rate constants relative to those for addition to styrene. Errors are the standard deviation from mean. [b] The absolute rate constant for *tert*-butoxy β-scission in benzene solvent is ca. 10^5 s^{-1} at 60 °C[8] (this rate is solvent dependent—see text). Therefore, the absolute rate constants for the other reactions of *tert*-butoxy radical under these conditions may be estimated by multiplying the numbers in the table by 10^6 M^{-1} s^{-1}. The conversion factors for methyl (Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, pp 37–112) and phenyl[21] radical reactions are ca. 10^5 and 10^8 M^{-1} s^{-1}, respectively. [c] Abstraction of allylic hydrogen. [d] Yield of methyl radical products not determined. [e] Literature data at 65 °C (Asmus, K.-D.; Bonifacic, M. In *Landoldt-Bornstein, New Series, Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13b, pp 1–284). [f] Aromatic substitution. [g] Product not detected. [h] Other products not determined.

Table II
Relative Yields (%) of Products from Decomposition of Di-*tert*-butyl Peroxalate in 10% (v/v) Styrene–MMA in Benzene at 60 °C

product	X_{MMA}[a] 0.84	0.53	0.19
1a	30.3	13.4	3.7
2	13.6	6.0	1.7
3	1.5	0.7	0.4
4a	30.6	63.0	81.1
6b	18.5	13.5	10.8
1b	2.9	1.3	0.5
4b	0.3	0.6	0.6
6c	0.1	0.09	0.06
1c	1.8	0.8	0.2
4c	0.3	0.6	0.9

[a] Mole fraction of total monomer.

Table III
Relative Yields (%) of Products from Decomposition of Di-*tert*-butyl Peroxalate in 10% (v/v) Styrene–MMA in Acetone at 60 °C

product	X_{MMA}[a] 0.84	0.53	0.19
1a	14.8	7.6	2.3
2	8.3	4.2	1.2
3	1.0	0.7	0.1
4a	16.2	38.5	53.9
6b	21.1	17.1	16.6
1b	3.1	1.7	0.6
4b	0.3	0.8	1.1
6d	34.9	28.8	23.5
1d			
4d	0.2	0.5	0.6

[a] Mole fraction of total monomer.

Table IV
Relative Yields (%) of Products from Decomposition of Di-*tert*-butyl Peroxalate in 10% (v/v) Styrene–MMA in Butan-2-one at 60 °C

product	X_{MMA}[a] 0.85	0.52	0.17
1a	5.6	3.1	1.0
2	3.1	1.7	0.5
3	0.3	0.3	0.1
4a	6.1	16.0	24.6
6b	7.0	6.5	6.0
1b	1.1	0.7	<0.1
4b	0.1	0.3	0.4
6e	2.7	2.2	2.0
6f + 6g[b]	74.1	69.1	65.3

[a] Mole fraction of total monomer. [b] Ratio of **6f**:**6g** is ca. 6:1.

Table V
Relative Yields (%) of Products from Decomposition of Di-*tert*-butyl Peroxalate in 10% (v/v) Styrene–MMA in Toluene at 60 °C

product	X_{MMA}[a] 0.85	0.52	0.18
1a	6.6	3.7	1.0
2	3.0	1.6	0.4
3			
4a	6.5	17.6	27.1
6b	3.3	3.0	3.2
1b	0.3		
4b		0.2	0.2
6h	80.0	73.9	68.1

[a] Mole fraction of total monomer.

tetrachloride as the reference reaction. Their data indicate a somewhat higher relative reactivity of 1:3.17 at 60 °C. Dickerman et al.[20] report a relative reactivity of 1:1.25 at 25 °C. These workers compared the reactivity of styrene and MMA to that of methacrylonitrile in competition experiments carried out in aqueous solution (phenyl radicals from diazonium salt by Meerwein reaction).

Finally, Scaiano and Stewart[21] have recently measured the absolute rate constants for phenyl radical addition to styrene and MMA in freon 113 at 25 °C (radicals generated by photolysis of either benzoyl peroxide or iodobenzene). The rate constants determined were (1.1 ± 0.1) × 10^8 and (1.8 ± 0.3) × 10^8, respectively, and the relative reactivity of the two monomers should thus lie between 1:1.5 and 1:1.75.

We find that the relative reactivity of phenyl radicals toward MMA vs styrene is solvent-dependent (see Table

Table VI
Relative Yields (%) of Products from Decomposition of Di-*tert*-butyl Peroxalate in Styrene–MMA at 60 °C

	X_{MMA}[a]		
product	0.83	0.52	0.18
1a	37.9	14.5	3.7
2	17.5	5.8	1.9
3	1.0	0.4	0.4
4a	40.6	76.0	92.4
6b	1.5	2.0	0.7
1b	1.2	0.8	0.2
4b	0.2	0.5	0.7

[a] Mole fraction of total monomer.

Table VII
Relative Yields (%) of Products from Decomposition of 2-(Phenylazo)-2-methylpropane in 10% (v/v) Styrene–MMA (X_{MMA} = 0.52) in Solvents at 60 °C

	solvent			
product	benzene	acetone	MEK	toluene
1c	49	46	40	44
2	<1	<1	<1	<1
4c	38	41	32	40
5	<1	<1	<1	<1
6c	7	7	4	4
abs solv	*a*	6[b]	24[c]	9[d]
arom subst	6[e]			3[f]
1c/**4c**	1.12	1.27	1.26	1.11

[a] Included in **6c**. [b] Compound **6d**. [c] Compounds **6e–g**. [d] Compound **6h**. [e] Biphenyl. [f] Compounds **7**.

Table VIII
Rates of Disappearance of Alkoxyamines (1) at 60 °C

	% loss with 0.01 M nitroxide			% loss with no nitroxide		
	2 h	4 h	16 h	2 h	4 h	16 h
1a	3	6	12	2	5	21
1d	3	7	23	12	23	65
1j	4	9	29	6	12	42

I) and that they are more reactive toward MMA in the ketone solvents. Furthermore, preliminary data show that both the relative reactivity of MMA and the magnitude of the fore-mentioned solvent effect are enhanced at lower temperatures. For this reason it is not profitable at this stage to discuss the small differences between the various literature data and between those data and our present results.

B. Solvent Effects and Monomer Relative Reactivity. It is evident from Table I that the relative rate constants for the reactions of *tert*-butoxy, methyl, and phenyl radicals are medium-dependent. For the case of phenyl (and perhaps methyl) radicals the relative rate of addition to methyl methacrylate vs styrene is slightly enhanced in the ketone solvents over what is observed in the aromatic solvents while for *tert*-butoxy radicals the relative rate of addition is slightly reduced.

The origins of these small solvent effects can only be speculated on at this stage. It is pertinant that *tert*-butoxy radicals are usually regarded as slightly electrophilic[5,22] while simple carbon-centered radicals are slightly nucleophilic.[23] Thus one possibility is that the solvent effects can be ascribed to the ability of the more polar (ketone) solvents to stabilize a polar transition state[24] or a polar form of the radical.[25] However, it is desirable that the effects of solvent on the reactions of radicals with more pronounced philicity (e.g. benzoyloxy, *tert*-butyl) and a wider range of solvents be investigated before any definite conclusions are drawn.

C. Solvent Effects and Regioselectivity. Whereas the reactions of methyl and phenyl radicals with MMA (and styrene) are relatively regioselective, giving at least 98% tail addition,[26] *tert*-butoxy radicals give substantial amounts of abstraction with MMA. Solvent effects on the regioselectivity of the reaction of *tert*-butoxy radicals with MMA have been discussed previously[1] when it was demonstrated that the fraction of addition to the double bond vs abstraction of an allylic hydrogen of MMA showed a significant solvent dependence. The fraction of addition vs abstraction with MMA which is observed in MMA–styrene mixtures is, not surprisingly, similar to that observed in MMA–benzene.[2]

D. Solvent Effects and Solvent-Mediated Initiation. As a consequence of the high propensity of *tert*-butoxy radical for H-atom abstraction as much as 80% of initiation may be by way of solvent derived radicals (see Tables IV and V). The precise amount will depend on the particular reaction conditions.

Even with benzene, a solvent which is usually thought of as being unreactive toward radicals, solvent derived products are observed (**1c**, **4c**—see Table II). That the latter products arise by phenyl radical initiation is evidenced by that fact that they appear in the same ratio as when phenyl radicals are generated directly from benzoyl peroxide or 2-(phenylazo)-2-cyanopropane.

There are two previous reports of *tert*-butoxy radicals reacting with benzene. Niki and Kamiya[27] determined that an aromtic hydrogen (benzene) had an apparent reactivity 8.75 times lower than a primary hydrogen (e.g. pentane). Brokenshire and Ingold[28] obtained an unstated yield of *tert*-butyl phenyl ether and diphenyl from the decomposition of di-*t*-butyl hyponitrite in benzene and took these products as evidence that *tert*-butoxy radical both abstracts from and adds to benzene.

In line with the latter report, we have found that trace amounts of *tert*-butyl phenyl ether are formed when di-*tert*-butyl peroxalate is decomposed in benzene in the presence of nitroxide. The nature of the reaction of *tert*-butyoxy radicals with benzene will be discussed in greater detail elsewhere.[29]

The rate constants for methyl radicals abstracting from monomer or solvent or undertaking aromatic substitution are substantially lower than those for reaction with double bonds (see Table I). Consequently, the reactions of methyl radicals with solvent are likely to be of little importance except when very high ratios of solvent to monomer are employed and are negligible under the conditions employed in the present series of experiments. The possibility of such reactions becoming important in free radical polymerizations carried to high conversion cannot however be ignored—see below.

While phenyl radicals undergo rapid reaction with solvent, their reactions with monomers are substantially faster[21] and under the conditions of our experiments abstraction from solvent is only of major importance with MEK and toluene. With the aromatic solvents (and styrene) significant yields of aromatic substitution are observed.

E. Solvent Effects and β-Scission. Another major effect of solvent on *tert*-butoxy radical reactions relates to the proportion of methyl radical products. There are two main influences: (a) Dilution of the reaction medium with a less reactive substrate (solvent) naturally results in an increase in the yield of methyl radicals. Thus a higher proportion of methyl radical products is observed if the medium is diluted with benzene yet no marked increase is seen with toluene as solvent. This is a consequence of the latter solvent's high reactivity toward *tert*-butoxy

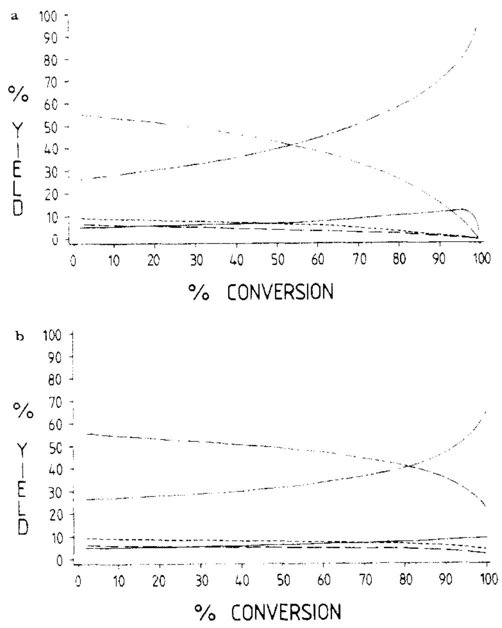


Figure 1. Results of computer simulation of copolymerization of methyl methacrylate and styrene 10% (v/v) in butan-2-one (refer text). Graph a shows the instantaneous distribution of the initiator-derived end groups and graph b the cumulative end group distribution expressed as a percentage yield. The following end groups are distinguished: $(CH_3)_3COCH_2CHPh$ (– – –); **8e–g** (– - - –); $(CH_3)_3COCH_2C(CH_3)(CO_2CH_3)$ (- - -); **2**, **3r** (–·–); CH_3 (—).

radical (compare Tables III, V, and VI). (b) The use of a more polar solvent enhances the rate of β-scission of *tert*-butoxy radial relative to addition or abstraction[1–5] (see Table I). Thus when MEK as opposed to toluene is used as solvent, a greater proportion of methyl radicals is formed (compare Tables IV and V) even though these solvents are of similar reactivity toward *tert*-butoxy radical (Table I).

F. Effects of Conversion. The stated aim of this study has been the estimation of the distribution of these end groups of poly(MMA-*co*-styrene) which are formed in initiation reactions. The radical trapping experiments described above can be directly translated to a picture of the end group distribution at zero conversion and may be considered a reasonable estimate at modest conversions. However, most polymers (including all those produced commercially) are prepared such that monomer conversion is maximized. As monomer is consumed, the reaction medium will change significantly, and, in light of the results discussed above, this may well influence the relative reactivity of the various substrates. However, the most obvious and probably the most important effect will be an increase in the proportion of solvent derived and methyl radical derived end groups as monomer is depleted. In addition, the monomer ratio will vary with conversion. The end result of these effects is that the end group distribution will change progressively during the copolymerization and the final end group distribution in a high conversion polymer may bear little resemblance to the initial distribution.

While it is a simple matter to predict qualitatively the effects that monomer depletion might have on the end group distribution, the number of variables involved renders a precise description extremely difficult. It would, in principle, be possible to carry out trapping experiments in the presence of preformed polymer and the appropriate monomer ratio so as to obtain information on the fate of the initiator at higher conversions. However, the number of experiments required to characterize a given polymerization is formidable.

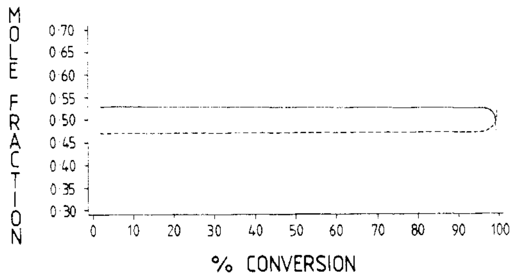


Figure 2. Results of computer simulation of copolymerization of methyl methacrylate and styrene 10% (v/v) in butan-2-one (refer text). Graph shows the variation of the mole fraction of residual monomer (MMA - - -; styrene —) with conversion.

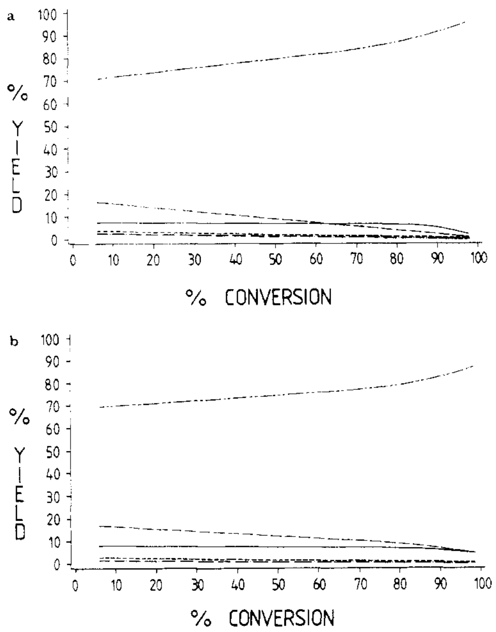


Figure 3. As Figure 1 but medium is 50% (v/v) butan-2-one.

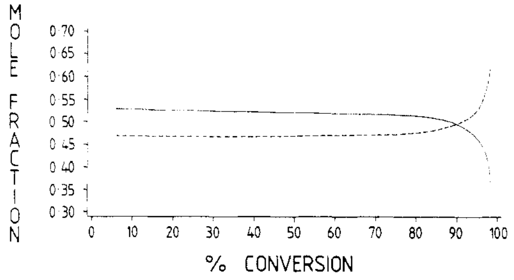


Figure 4. As Figure 2 but medium is 50% (v/v) butan-2-one.

In order to assess, in a more quantitative and less time-consuming manner, the variation in the end group distribution with conversion, a computer simulation of the copolymerization of MMA and styrene has been carried out by using the SOCK program.[30,31] The SOCK program was used to calculate the concentration–time dependence of all species involved in the copolymerization. The SAS program[32] was then employed to convert this to a concentration–conversion dependence and produce the graphs shown in Figures 1–4.

There is literature rate data enabling the estimation of the absolute rate constants for the reactions of *tert*-butoxy,[8] methyl,[33] and phenyl[21] radicals. However, absolute rate data is lacking for the reactions of the radicals derived by abstraction from monomer or solvent. For the purpose of the simulation it is assumed that all of the initiation reactions are fast ($>10^4$ M^{-1} s^{-1}) and, therefore, are not rate-determining. We do not take into account such processes as primary radical termination and transfer to initiator. The reaction of the initiator derived radicals with "dead" polymer is assumed to be negligible[34] as is any effect of medium viscosity on the rates.[35] The main limitation on the accuracy of the simulation is then the accuracy with which the literature reactivity ratios and rate data[36] are able to predict the variation in copolymer composition with conversion.

The propagation and termination rate constants employed are those used in our previous study of termination in styrene–MMA copolymerization[31] and are one of many sets of data that appear in the literature. We offer no justification for choosing these values over others. The precise values of these rate constants do not alter the general conclusions which we wish to draw re the dependence of the instantaneous distribution (Figures 1a and 3a) of initiator derived end groups on conversion. However, it should be noted that the cumulative end group distribution (Figures 1b and 3b) is very much a function of the molecular weight of polymer being formed at each stage of conversion and hence on the absolute values of the propagation and termination rate constants and the probable dependence of these parameters on conversion and chain length.

In order to separate out the effects of conversion on monomer composition from the other effects mentioned above and so simplify the interpretation of the data, we attempted to carry out the simulation at the "azeotrope monomer composition" [calculated according to $(f_1)_c = (1 - r_1)/(2 - r_1 - r_2)$]. However, it was found that the extent of monomer utilization in the initiation and termination reactions, which occurs at a different rate to that in the propagation reactions, was sufficient to cause a significant variation from this "azeotropic composition" after only 70% conversion (see Figure 2) for 10% monomers in solvent. While this situation can be improved if conditions are chosen such that higher molecular weight polymer is formed [lower initiator concentration, higher monomer concentration (see Figure 4)], we, nonetheless, conclude that it is not possible to carry out an azeotropic copolymerization to complete conversion. The differing relative reactivities of the two monomers toward the various initiating species may also influence the monomer sequence distribution at the chain ends and the molecular weight distribution.[37]

Figures 1 and 3 illustrate the effects of conversion on the distribution of end groups formed in initiation reactions for an "azeotropic" styrene–MMA copolymer prepared in 90% (v/v) butan-2-one (Figure 1) or 50% (v/v) butan-2-one (Figure 3) as solvent and with *tert*-butoxy radical initiation. Points to note are the following. (a) Even when high monomer concentrations are employed, if the polymerization is carried to high conversion, most end groups will be solvent derived. (b) The fraction of methyl end groups also increases with conversion. However, since methyl radicals have a measurable reactivity toward butan-2-one (see Table I), the production of these end groups peaks at ca. 95% conversion (Figure 1a) or ca. 70% conversion (Figure 3a).

Studies aimed at removing some of the limitations on the accuracy and/or confirming the results of the simulations by directly measuring the end group distribution (concurrently with the monomer ratio) as a function of conversion (by ^{13}C NMR and employing ^{13}C-labeled initiators[38]) are currently being undertaken.

Conclusions

The nature of the solvent employed in a polymerization reaction can have a profound effect on the distribution of end groups. Furthermore, if an alkoxy radical source is employed, solvent may become directly involved in the initiation process, and depending on the nature of the medium, most of the end groups may be solvent derived. Two solvents that see widespread use in industry (toluene and MEK) are particularly active in this respect.

As a polymerization proceeds and monomer is consumed, the percentage of initiation that involves the intermediacy of solvent-derived radicals will increase. The fraction of primary radicals which undergo β-scission will also increase with conversion. The manner in which the changing nature of the reaction medium (with conversion) effects the nature and efficiency of the initiation reaction in homo- and copolymerization can be estimated by computer simulation using the data from the trapping experiments as a basis for the extrapolation. However, further work is needed before all variables can be taken into account.

Experimental Section

HPLC was conducted using a Dupont 8800 liquid chromatograph equipped with a variable wavelength UV detector set at 270 nm and coupled to a Trivector Trilab Model II data station. Dupont Zorbax 5u ODS (4.6 mm × 250 mm) or a Beckman Ultrasphere ODS column (10 mm × 250 mm) were employed with methanol/acetonitrile/water mixtures as eluant. GLC was performed on a Varian Vista 6000 gas chromatograph equipped with a flame ionization detector, which was connected to the same data station. A 2 m × 2 mm, 0.2% Carbowax 1500 on Carbopack C (80–100 mesh) column was employed.

Monomers were purified by passage through neutral alumina and were fractionated immediately before use.

Competition Experiments. Weighed amounts of initiator, 1,1,3,3-tetramethylisoindolin-2-yloxy,[10] and the monomer were placed in a volumetric flask that was then made up with the solvent to be used. Appropriate amounts of the two stock solutions thus prepared were placed in reaction vessels that were degassed by three freeze–thaw cycles, then sealed under vacuum, and heated in a waterbath at 60 °C for 1.5 h (reactions with *tert*-butyl peroxalate or benzoyl peroxide) or photolyzed in a thermostated reaction vessel in a Rayonet photochemical reactor (reactions with 2-(phenylazo)-2-cyanopropane[39]) employing 360-nm lamps for 1 h (reactions at 60 °C) or 16 h (reactions at 10 °C).

The yield from the photolyses were found to be strongly temperature dependent, and reactions carried out at 10 °C gave only poor (ca. 30% after 16 h) yields. Longer reaction times gave rise to unidentified byproducts.

The reaction mixtures were anlayzed by GLC for monomer composition and by HPLC. Reactions carried out in bulk or involving >50% (v/v) styrene needed to be concentrated before HPLC analysis could be performed.

Compounds **6f** and **6g** were not resolved by HPLC. Accordingly the mixture of these materials was isolated by preparative HPLC, and the ratio of **6f** and **6g** was estimated by ^{1}H NMR as ca. 6:1.

The results of these experiments are shown in Tables II–VII.

Registry No. (MMA)(Sty) (copolymer), 25034-86-0; MMa, 80-62-6; Sty, 100-42-5; t-Bu$^\bullet$, 3141-58-0; Me$^\bullet$, 2229-07-4; Ph$^\bullet$, 2396-01-2.

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Notes

Effect of Sequence Distribution on the Critical Composition Difference in Copolymer Blends

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Introduction

Since the early theoretical work of Scott,[1] it has been known that two statistical AB copolymers, which have the same chain length but differ in composition, are not necessarily miscible in all proportions. Scott predicted that binary copolymer mixtures would be characterized by a maximum tolerable difference in chemical composition (in the following denoted by Δ) beyond which they are only partly miscible. This conclusion was experimentally verified by Molau[2] and Locatelli and Riess[3] for copolymers of styrene and acrylonitrile (SAN) and by Kollinsky and Markert[4,5] for various acrylic copolymers. However, the latter work also revealed that Δ depends on the chemical composition of one of the two copolymers in the mixture. This feature cannot be explained by Scott's theoretical analysis. However, it can be dealt with in a qualitatively correct way if the different constitutional repeat units are assigned different interacting surface areas.[6] In this way, if the B unit in a given copolymer can make more nearest-neighbor contacts per site than its A unit, we expect Δ to decrease with increasing A content. If, however, less contacts per site are possible, then Δ will increase with increasing A content. Calculations for different interacting surface area ratios show Δ to depend almost linearly on the composition of one of the copolymers in the mixture.[7] However, from the work of Kollinsky and Markert, it is clear that large deviations from linearity are possible, a behavior that remains unexplained by previous theories. In this paper, we will show that it is possible to explain these deviations from linearity by introducing sequence distribution effects. The starting point is the model developed by Balazs et al.,[8,9] which, for a copolymer of fixed composition, can examine the effects of sequence distribution on both copolymer/homopolymer[8] and copolymer/copolymer[9] miscibility.

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