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The effects of some phenyl derivatives of propene upon radical polymerizations

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An examination has been made of the effects of 1-phenyl-1-propene, (β-methylstyrene) (BMS), 3-phenyl-1-propene (allylbenzene) (AB), 1,2-diphenyl-1-propene (1,2-DPP) and 1,3-diphenylpropene (1,3-DPP) on the radical polymerizations of methyl methacrylate (MMA) and styrene (STY) at 60°C. Transfer constants have been found by the method depending on analyses of polymers for end-groups derived from the initiator, ^{14}C-labelled azobisisobutyronitrile (AIBN). The procedure requires information on the relative importance of disproportionation and combination in the bimolecular termination processes during the polymerizations. End-group analyses on polymers made using ^{14}C-AIBN without additives indicate that 10% of the terminations occur by combination for MMA; the corresponding proportion for STY is 75%. AB and especially 1,3-DPP are powerful transfer agents and retarders. BMS retards the polymerizations but it appears to become incorporated inside the polymer molecules instead of forming end-groups, as it would if it functioned as a transfer agent. 1,2-DPP has almost no effect on the rates of polymerization and is only a weak transfer agent. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

A new procedure for determination of transfer constants depends upon analyses of polymers for end-groups derived from the initiator used in their preparation[1]. The treatment can be extended to transfer agents which cause retardation of polymerizations[2]. Results have been reported for substances of various types giving rise to degradative transfer, namely diphenylpicrylhydrazine, 1,3-diphenylpropene, fluorene[2] and iodoform[3]; they were used as additives during polymerizations of methyl methacrylate (MMA) and styrene (STY) at 60°C with azobisisobutyronitrile (AIBN) as initiator and benzene as diluent. It was pointed out[4] that it might be instructive to extend the study of isomers of derivatives of propene as transfer agents. The present paper refers to comparisons between 1-phenyl-1-propene (β-methylstyrene) (BMS) and 3-phenyl-1-propene (allylbenzene) (AB) and between 1,2-diphenyl-1-propene (1,2-DPP) and 1,3-diphenylpropene (1,3-DPP).

The best known case of degradative transfer to an allyl compound is probably that of transfer to monomer during the radical polymerization of allyl acetate[5]. Bartlett and Tate[6] showed that abstraction of hydrogen occurs mainly from the methylene group of the monomer, giving a stabilized allylic radical which is sluggish in its reaction with monomer so being responsible for inefficient re-initiation and therefore rather slow polymerization giving polymer of low molecular weight. It was subsequently shown[7,8] that isopropenyl acetate behaves in much the same way as allyl acetate. There is little published information on transfer constants for allyl compounds of the types now being considered; values have, however, been quoted[9] for allylbenzene in the polymerization of MMA at 60°C and

that of STY at 100°C. Certain allyl compounds such as $CH_2=C(CO\cdot O\cdot CH_3)\cdot CH_2\cdot S\cdot C(CH_3)_3$ have been reported to act as efficient transfer agents by an addition–elimination mechanism[10] and the process has been applied to the preparation of macromers[11].

Limited data are available[12] on copolymerizations involving compounds such as AB; generally for STY and MMA (monomer-1), the monomer reactivity ratio r_1 is large (say in the region of 20) whereas r_2 is close to zero. For the systems used in the present study of transfer to derivatives of propene, the concentrations of monomer and transfer agent are such that there can be very little incorporation of the latter by growth reactions. Polymers of MMA prepared in the presence of unsaturated transfer agents have, however, been examined by n.m.r. to check on the extent to which the additive becomes incorporated in polymer; the final purification of each polymer used in these tests was performed by precipitation in methanol from solution in a non-aromatic solvent.

The determination of transfer constants by consideration of end-groups derived from the initiator is based upon the equation

$$\frac{k_f[T]}{k_p[M]} + \frac{k_s[S]}{k_p[M]} + \frac{k_m}{k_p} = \frac{2-2n+nf}{2n\nu} \quad (1)$$

where [T], [S] and [M] are respectively the concentrations of transfer agent, diluent and monomer in the polymerizing system, n is the average of the numbers of initiator fragments in the resulting polymer molecules, ν is the kinetic chain length in the polymerization, and f is the fraction of the bimolecular terminations occurring by combination. Generally the derived values of k_f/k_p need modification if the transfer is degradative[2]. The three terms on the left-hand side of equation (1) arise from transfer to an additive, to diluent and to monomer respectively. In previous work,

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transfers to monomer and diluent were regarded as negligible compared with transfer to the additive. Transfers to initiator and to polymer have been omitted from the treatment because of the direct evidence[13] that transfer to AIBN is very rare during polymerizations of MMA and STY at 60°C and the fact that transfer to polymer normally does not affect n and ν[4].

It seems now to be accepted that the dominant modes of termination for MMA and STY at 60°C are disproportionation and combination, respectively, but doubt still remains about the exact values of f. This problem and the possible effects of transfers to benzene and monomer have been reconsidered.

EXPERIMENTAL

All procedures have been described previously[1,2] and all materials were prepared and/or purified by standard procedures. Polymerizations were performed anaerobically at 60°C with benzene as diluent; for most of them, the rate was measured dilatometrically. Conversions did not exceed 7%. Polymers were recovered by precipitation in methanol and those prepared with ^{14}C-AIBN were purified by three such precipitations from solutions in toluene. Activities of ^{14}C-labelled materials were measured by scintillation counting of solutions. Average molecular weights of polymers were found by size exclusion chromatography. The equipment used for this purpose consisted of a Waters 510 pump, Gilson 234 auto-injector, Polymer Laboratories 'PL gel' mixed 'B' columns (3 × 30 cm) and an Erma 7512 refractive index detector. Data were acquired and analysed with a Polymer Laboratories data station and 'PL Caliber' software. The columns were calibrated with narrow distribution polySTY and polyMMA standards. Polymer solutions (0.25% w/v) were prepared and subsequently eluted with tetrahydrofuran. Toluene was used as a marker to correct for variations in flow-rate.

RESULTS AND DISCUSSION

Table 1 gives information on the experiments performed to allow re-evaluation of f for polymerizations of MMA and STY at 60°C. The initiator was labelled with carbon-14 so that for each polymer the number of monomeric units associated with one incorporated initiator fragment could be

found by comparison of the specific activities of the initiator and the polymer. That number is ν for the polymerization provided that each act of initiation led to the inclusion in the polymer of an initiator fragment $(CH_3)_2C(CN)-$ as an end-group and that no initiator fragments entered the polymer by other processes. For specific activities in $Bq\ g^{-1}$, ν is given by $82a_i/100a_p$ for polyMMA and by $82a_i/104a_p$ for polySTY where a_i and a_p are the specific activities of AIBN and the polymer respectively; n is then found as $\overline{DP}/\nu$.

For MMA and STY, the mean values of n are 1.01 ± 0.06 and 1.55 ± 0.07 respectively without systematic dependence on the concentration of monomer or that of AIBN or on the position of the labelling atom in the molecule of the initiator. The scatter of results can be attributed to experimental uncertainties perhaps mainly in the determinations of $\overline{M}_n$. From the relationship

$$n = 2/(2 - f)$$

it is found that f is 0.02 for MMA and 0.71 for STY but these quantities may be slight underestimates because of neglect of effects of transfers to monomer and diluent. The latter processes were disregarded in early work[14] on the combination/disproportionation problem, benzene being selected as diluent for the polymerizations because of its very low reactivity in transfer processes. The transfer constants for benzene in the polymerizations at 60°C of MMA and STY have been selected[15] as 4×10^{-6} and 2×10^{-6} respectively and the corresponding quantities for transfer to monomer[16] as 1×10^{-5} and 6×10^{-5}.

Equation (1) has been used to obtain guidance on the effects of these transfer processes on the evaluation of f for the monomers. It is supposed that, for an 'average' of the polymerizations of MMA referred to in *Table 1*, ν is 1330 and n is 1.01; if f is taken as 0.05, 0.10 or 0.20 in turn, $(2 - 2n + nf)/2n\nu$ becomes 1×10^{-5}, 3×10^{-5} or 7×10^{-5}. In the 'average' polymerization, [benzene]/[monomer] is approximately four so that $k_s[S]/k_p[M]$ may be 1.6×10^{-5}; the sum of $k_s[S]/k_p[M]$ and k_m/k_p can be taken as 2.6×10^{-5} which is consistent with f being 0.10 for MMA and n being 1.05 if transfers to monomer and diluent do not occur. In a similar treatment for STY, [benzene] and [monomer] can be taken as equal so that $k_s[S]/k_p[M]$ may be 2×10^{-6} and its sum with k_m/k_p is 6.2×10^{-5}. Taking ν as 330, n as 1.55 and f as 0.75, $(2 - 2n + nf)/2n\nu$ becomes 5.9×10^{-5} so that

Table 1 Polymerizations of methyl methacrylate and styrene

No.	[Monomer]	10^2[AIBN]	Activity of polymer (Bq g^{-1})	$10^{-3}\overline{M}_n$ of polymer	ν	n
1	1.97 m	0.62 a	275	105.4	979	1.08
2	2.15 m	1.05 b	1530	69.5	701	0.99
3	2.70 m	0.71 a	217	120.0	1242	0.97
4	3.15 m	0.70 b	845	135.4	1270	1.07
5	5.64 m	0.72 a	110	228.0	2447	0.93
6	3.72 s	0.79 a	935	45.3	277	1.59
7	4.16 s	1.10 b	4167	41.9	248	1.63
8	4.16 s	2.90 b	6870	22.4	150	1.43
9	5.30 s	1.15 a	712	58.9	364	1.57
10	8.81 s	1.15 a	432	93.9	600	1.52

m, methyl methacrylate; s, styrene
a, AIBN labelled in CH$_3$ groups, activity = 32.8×10^4 Bq g^{-1}
b, AIBN labelled in CN groups, activity = 130.8×10^4 Bq g^{-1}
ν, kinetic chain length in the polymerization
n, average number of initiator fragments per polymer molecule

Table 2 Experiments involving allylbenzene and β-methylstyrene

No.	[Monomer]	10^2[AIBN]	[Additive]	$10^5 R_p$	Activity	$\bar{M}_n/10^3$
11	2.01 m	0.31 c	0.42 AB	2.60	212	80.1
12	2.01 m	0.31 c	0.32 AB	2.91	193	89.0
13	2.15 m	0.64 b	0.86 AB	3.45	1578	53.3
14	2.50 s	0.24 c	0.43 AB	0.71	618	41.3
15	2.13 s	0.34 c	0.12 AB	–	898	33.1
16	2.79 s	0.81 c	0.43 AB	1.48	1072	25.1
17	2.01 m	0.86 c	0.075 BMS	3.36	420	68.6
18	2.01 m	0.86 c	0.11 BMS	2.73	602	64.2
19	2.15 m	0.88 b	1.75 BMS	1.26	4600	31.6
20	2.88 m	1.00 b	1.34 BMS	2.55	3283	52.0
21	3.00 m	1.04 c	0.075 BMS	5.45	375	91.4
22	2.50 s	0.80 c	0.050 BMS	1.32	1245	28.1
23	2.50 s	0.80 c	0.090 BMS	1.32	1325	26.2
24	2.66 s	3.10 b	1.34 BMS	2.36	13633	12.5
25	2.79 s	0.80 c	0.075 BMS	1.45	1128	34.1

Derived quantities

No.	ν	n	$10^6 R_i/$[AIBN]	$10^3(k_f/k_p)$	Monomer/additive
11	981	0.82	8.55	1.31	m/AB
12	1070	0.83	8.73	1.48	m/AB
13	680	0.78	7.91	1.23	m/AB
14	327	1.21	9.15	3.60	s/AB
15	222	1.43	–	5.87	s/AB
16	186	1.30	9.83	4.96	s/AB
17	495	1.39	7.90	–	m/BMS
18	345	1.86	9.19	–	m/BMS
19	233	1.36	6.14	–	m/BMS
20	327	1.59	7.80	–	m/BMS
21	554	1.65	9.46	–	m/BMS
22	160	1.69	11.56	–	s/BMS
23	151	1.67	10.93	–	s/BMS
24	76	1.58	10.02	–	s/BMS
25	177	1.85	10.24	–	s/BMS

R_p = rate of polymerization in mol dm^{-3} s^{-1}
Activity = activity of polymer in Bq g^{-1}
$\bar{M}_n$ refers to polymer
m, methyl methacrylate; s, styrene
b, AIBN labelled in CN groups; activity = 130.8×10^4 Bq g^{-1}
c, AIBN labelled in CH$_3$ groups; activity = 25.3×10^4 Bq g^{-1}
ν, kinetic chain length in polymerization
n, average number of initiator fragments per polymer molecule
$R_i/$[AIBN] given in s^{-1}

the selected value of f seems to be reasonable giving n as 1.60 for a system with no transfer; the value of f used previously for STY was 0.70 corresponding to an uncorrected value for n of 1.54.

The effects of transfers to diluent and monomer seem to be very small when considering polymerizations of MMA and STY in benzene but even small changes in f may affect significantly the calculation of a transfer constant in a case where n for the polymer prepared in the presence of the transfer agent is close to that for the corresponding polymer prepared in the absence of the agent. The greatest uncertainty in the value of a transfer constant arises, however, in doubt about the exact value of n for a polymer prepared using the transfer agent.

Table 2 refers to polymerizations performed in the presence of AB or BMS and to the resulting polymers. The rates of polymerization (R_p) were used to calculate rates of initiation (R_i) as R_p/ν and values of $R_i/$[AIBN] are

quoted. The transfer constants shown in the table were calculated by means of equation (1).

AB and BMS retard the polymerization of MMA, the latter additive being the more effective. For MMA at 2.01 mol dm^{-3} and AIBN at 0.70×10^{-2} mol dm^{-3} the presence of AB or BMS at 0.25 mol dm^{-3} causes R_p to fall to 80 or 55% respectively of that in the absence of additive. The retardation is much less marked when STY replaces MMA.

Polymers of MMA were prepared using AIBN and either AB or BMS at a concentration such that [additive]/[MMA] was close to 0.4; they were purified by precipitation from dimethylformamide and their ^{13}C n.m.r. spectra were recorded at 100 MHz on a Bruker WH400 instrument. There were only very faint signals attributable to aromatic carbon atoms. It was concluded that less than one AB or BMS unit was incorporated for 50 units of MMA. The low level of incorporation is insufficient to affect significantly

Table 3 Experiments involving diphenylpropenes

No.	[Monomer]	10^2[AIBN]	[Additive]	$10^5 R_p$ (mol dm^{-3} s^{-1})	Activity of polymer (Bq g^{-1})	$\bar{M}_n/10^3$ of polymer
26	2.78 m	0.70 a	0.18 h	4.15	337	77.6
27	4.11 m	1.33 b	1.14 h	4.28	2030	42.7
28	3.70 s	0.52 a	0.087 h	1.67	828	45.7
29	3.80 s	1.51 b	0.45 h	2.02	6600	18.0
30	1.85 m	0.28 c	0.083 j	–	178	114.7
31	2.15 m	1.11 b	0.30 j	7.14	1422	87.8
32	2.66 s	2.82 b	0.60 j	2.60	10733	16.3
33	2.82 s	0.89 c	0.18 j	–	1345	25.5

Derived quantities

No.	Monomer/ additive	ν	n	$10^6 R_i$/[AIBN] in s^{-1}	$10^2(k_f/k_p)$
26	m/h	798	0.97	7.42	0.159
27	m/h	528	0.81	6.09	0.194
28	s/h	312	1.41	10.04	1.21
29	s/h	160	1.08	8.37	1.59
30	m/j	1166	0.98	–	0.137
31	m/j	755	1.16	8.53	–
32	s/j	96	1.63	9.60	–
33	s/j	148	1.66	–	–

m, methyl methacrylate; s, styrene
h, 1,3-diphenylpropene; j, 1,2-diphenyl-1-propene
a, AIBN labelled in CH_3 groups; activity = 32.8×10^4 Bq g^{-1}
b, AIBN labelled in CN groups; activity = 130.8×10^4 Bq g^{-1}
c, AIBN labelled in CH_3 groups; activity = 25.3×10^4 Bq g^{-1}
ν, kinetic chain length in the polymerization

the measurements of $\bar{M}_n$ based on the view that the polymers were essentially homopolymers of MMA.

The means of the values of k_f/k_p for AB with MMA and STY are 1.34×10^{-3} and 4.81×10^{-3} respectively; the differences between the individual results for a particular monomer are undoubtedly largely due to experimental errors. These values of k_f/k_p are reduced if allowance is made for transfers to monomer and diluent but the changes are small. As explained already, the sum of $k_s[S]/k_p[M]$ and k_m/k_p may be in the region of 2.6×10^{-5} for the experiments involving MMA and 6.0×10^{-5} for those with STY; these quantities are appreciably less than the values of $(2 - 2n + nf)/2n\nu$ in all cases. In view of larger uncertainties caused by other effects, the small corrections for transfers to monomer and diluent are not made.

Values of R_i/[AIBN] are similar to the expected value of about 10^{-5} s^{-1} for the reactions involving STY, suggesting that there were no anomalies in the initiation process for the polymerizations. In the case of MMA, values of R_i/[AIBN] were smaller, particularly when $\bar{M}_n$ for the recovered polymer was low; the results are consistent with those found for many other systems and they can be explained by loss of some at least of the smaller polymer molecules during the recovery and purification by precipitation in methanol. Again there is no need to suppose that the initiation process is appreciably affected by the presence of either AB or BMS.

For a system in which the radical derived from the transfer agent either re-initiates by reaction with monomer or terminates by reaction with a polymer radical, the transfer constant calculated from equation (1) should be increased by the factor $(f - fe + e)^{-1}$ where e is the efficiency of re-initiation. The values of f for MMA and STY are known

but those of e are not. Clearly e for STY is greater than for MMA because the retardation caused by AB is appreciably less severe for the former monomer. Taking f for STY as 0.75 and e also as 0.75, the correcting factor becomes 1.06 so that the corrected mean value of k_f/k_p becomes 5.1×10^{-3}. For a monomer such as STY for which termination is largely by combination, changing the value selected for e does not greatly affect the correcting factor; for e being 0.85 or 0.65, the factors are 1.04 and 1.10 respectively leading to corrected values of k_f/k_p of 5.0×10^{-3} or 5.3×10^{-3}. For MMA, f is 0.10; if e is taken as 0.20, the correcting factor is 3.56 so that the revised mean value of k_f/k_p is 4.8×10^{-3}, i.e. similar to that for STY with AB. When f is small, changes in e have quite large effects on $(f - fe + e)^{-1}$; in the case of MMA, values of 0.10 and 0.30 for e lead respectively to factors of 5.26 and 2.70 and the revised transfer constant becomes 7.0×10^{-3} or 3.6×10^{-3}.

It may not be justified to suppose that e has the same value for all cases involving a particular pair of monomer and transfer agent. The balance in the competition between monomer and growing radicals (P·) for capture of the transfer radicals must depend on the relative concentrations of those species, in the sense that e must increase to some extent if [M]/[P·] is increased. [P·] is proportional to R_p/[M] so that e becomes somewhat larger as $[M]^2/R_p$ is increased and consequently the factor $(f - fe + e)^{-1}$ becomes smaller. The results in *Table 2* are, however, not precise enough for this treatment to be tested.

It is likely that abstraction of hydrogen from AB leads to the stabilized allylic radical PhCH·CH:CH$_2$, so accounting for the degradative nature of the transfer. If BMS acts as a degradative transfer agent, it would probably give the allylic radical ·CH$_2$·CH:CHPh which is effectively the same

radical as that probably formed from AB. The results for n (see *Table 2*) show that the action of BMS must be quite different from that of AB. For samples of polyMMA prepared in the presence of BMS, n is in the region of 1.50 and the corresponding quantities for polySTY also exceed those for polymers prepared in the absence of additive. The results for n could be explained if BMS adds to a growing radical to give P·CHMe·CHPh which then does not engage in further growth reactions but reacts, mainly by combination even in the case of MMA, with another growing radical to give P·CHMe·CHPh·P. The overall process formally resembles that proposed for the action of p-benzoquinone as a retarder for the polymerization of MMA[17].

Experiments involving 1,3-DPP or 1,2-DPP are referred to in *Table 3* which contains information corresponding to that in *Table 2*. The 1,3-isomer is a stronger retarder for the polymerization of MMA than either AB or BMS; for MMA at 2.78 mol dm^{-3}, AIBN at 0.70 × 10^{-2} mol dm^{-3} and 1,3-DPP at 0.25 mol dm^{-3}, R_p is only 30% of that for the corresponding system without additive. The retardation is appreciably less marked when STY replaces MMA. 1,2-DPP has only slight effects on R_p for MMA and STY. The ^{13}C n.m.r. spectra of polymers of MMA, prepared using AIBN, show that there is very little incorporation of either 1,2- or 1,3-DPP.

The results of single determinations of transfer constants for the isomers of DPP have been given[4] but those for STY need revision because f was taken as 0.70 instead of 0.75, the value now favoured. The means of the present values of k_f/k_p are 1.40 × 10^{-2} for STY/1,3-DPP and 1.76 × 10^{-3} for MMA/1,3-DPP. These transfer constants need revision upwards because of the degradative transfers. The correcting factor $(f - fe + e)^{-1}$ must be much smaller for STY than for MMA for two reasons; f for STY is greater than for MMA and e must be appreciably smaller for MMA than for STY in view of the more pronounced retardation with the former monomer. Taking both f and e as 0.75 for STY/1,3-DPP, k_f/k_p is corrected to 1.48 × 10^{-2}. For MMA, f is 0.10; if e is 0.10, k_f/k_p becomes 9.78 × 10^{-3} or 1.76 × 10^{-2} if e is zero. It appears that the transfer constants for MMA and STY with 1,3-DPP are similar in magnitude, as for the monomers with other hydrocarbons; it is to be noted, however, that k_p for MMA is larger than that for STY so that, in cases such as 1,3-DPP, the polyMMA radical abstracts hydrogen rather more readily than the polySTY radical.

Transfer constants for 1,2-DPP must be quite small because the values of n for three of the four polymers slightly exceed those for the corresponding polymers derived from systems from which the additive was absent; n for polymer no. 30 is such that the derived transfer constant cannot be regarded as reliable.

In principle, the derivatives of propene considered here might engage in transfer by the addition–fragmentation process but it seems rather unlikely. The radicals which might be formed by addition of AB, BMS, 1,3-DPP or 1,2-DPP to a growing centre seem not to satisfy the conditions necessary for fragmentation; the pendant groups do not contain weak bonds and they could not yield stabilized radicals which would be inefficient in re-initiation. The addition stage occurs for BMS but the product radical reacts with another growing centre instead of fragmenting. It is possible that a similar process might occur to some extent with the other transfer agents but there is no evidence to that effect.

It would be interesting to consider 2-phenylpropene (α-methylstyrene) as a transfer agent; it is, however, impracticable to examine it by the method used here because of its capacity to engage in copolymerization although ceiling temperatures for its homopolymerization are comparatively low. There are no indications that transfer to monomer is particularly important for α-methylstyrene or certain other monomers with α-methyl groups, such as MMA and methacrylonitrile which can be regarded as 2-substituted propenes; there is no evidence that transfer to monomer, when it occurs, is degradative. It was suggested[4] that substitution at the 2-position in propene interferes with the delocalization and stabilization of the radical which would be formed by abstraction of hydrogen. This hypothesis would also provide an explanation for 1,2-DPP being much less reactive than 1,3-DPP as a transfer agent although the 1,2-isomer is considerably the more reactive towards the benzoyloxy radical[18].

It is apparent that there are practical problems with the 'initiator fragment' method for determination of transfer constants. The difficulties seem to arise from uncertainties in the methods used at present for determination of n. It might be thought that losses of small polymer molecules during recovery of pure polymers might lead to errors. Such losses, however, do not of themselves spoil the measurements since the determinations of ν and $\bar{M}_n$ are made on samples of the same material; there may be small differences between the values of n and perhaps also those of f for the fractions of very low molecular weight and the corresponding quantities for the remainder of the polymer but the effects on the present studies are most probably very small.

The discovery of the unusual behaviour of BMS suggests that the new method will be particularly useful for detecting anomalous behaviour of an additive which appears to be functioning as a transfer agent. The effect could not have been detected by older procedures for determining transfer constants, namely that depending only on determinations of molecular weights of polymers and that based upon the analysis of polymers for incorporated transfer agent.

CONCLUSIONS

Polymers of methyl methacrylate (MMA), made by free radical polymerization at 60°C with azobisisobutyronitrile as initiator and benzene as diluent, contain 1.01 initiator fragments in the average polymer molecule; the corresponding number for polymers of styrene (STY) is 1.55. After making small allowances for transfers to monomer and benzene, it is deduced that 10% of the bimolecular terminations occur by combination during the polymerization of MMA and that the corresponding quantity for STY is 75%.

1,3-Diphenylpropene, 1-phenyl-1-propene and 3-phenyl-1-propene are powerful retarders of the polymerizations; 1,2-diphenyl-1-propene has little effect on the rates. The actions of these substances have been examined by analyses for initiator fragments incorporated in polymers prepared in their presence. When transfer occurs, the number of initiator fragments in the average polymer molecule is reduced below the number for the polymer prepared in the absence of additive; the magnitude of the effect depends upon the relative concentrations of monomer and transfer agent and on the transfer constant k_f/k_p. After making adjustments to allow for the degradative nature of the transfer processes, k_f/k_p for 1,3-diphenylpropene is 1.5 ×

10^{-2} for STY and 1.0×10^{-2} for MMA; the transfer constants for 3-phenyl-1-propene with STY and MMA are both 5.0×10^{-3}. The reactivity in transfer of 1,2-diphenyl-1-propene is much smaller probably because loss of a hydrogen atom from the methyl group does not give a highly stabilized radical. The behaviour of 1-phenyl-1-propene is anomalous in the sense that it causes the number of initiator fragments in the average polymer molecule to be significantly higher than for cases in which additive is absent from the polymerization. It appears that the additive becomes incorporated within the polymer chains and not at the ends as it would be if it functioned as a normal transfer agent.

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