

The spontaneous polymerization of methyl methacrylate: 6. Polymerization in solution: participation of transfer agents in the initiation reaction*

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(Received 30 December 1982)

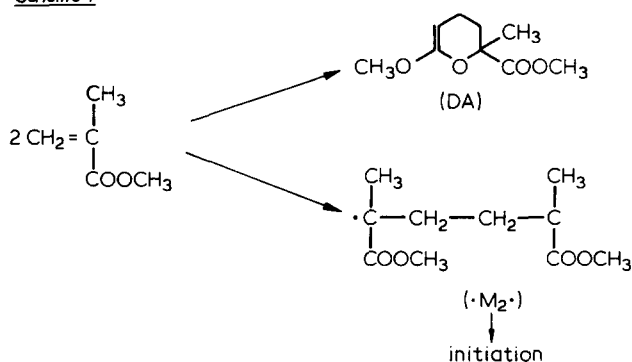
The rate of the spontaneous polymerization of methyl methacrylate is strongly affected by the addition of transfer agents. The kinetics are interpreted in terms of a participation of transfer agents in the initiation step. In this, the original biradical, $\cdot M_2\cdot$, which is produced from two monomer molecules and which has a high self-termination probability, is converted into polymerizable monoradicals. Increase in the concentration of a strong transfer agent leads to double-transferred compound HH1, the mass spectral identification of which is to be regarded as first direct evidence for the existence of biradical $\cdot M_2\cdot$.

Keywords Methyl methacrylate; spontaneous polymerization; initiation mechanism; dimers; biradicals; transfer

INTRODUCTION

Whereas the spontaneous polymerization of styrene is well documented¹, very few results on the kinetics of the spontaneous polymerization of methyl methacrylate (MMA) and related compounds have been published². The Diels–Alder-initiation mechanism proposed for the thermal polymerization of styrene by Mayo³ is not applicable to MMA, due to the missing tendency of the hetero-analogous Diels–Alder compound (DA) to form an aromatic hydrocarbon. Therefore Pryor¹ adapted an initiation mechanism *via* a dimeric biradical $\cdot M_2\cdot$ postulated earlier for the spontaneous polymerization of styrene by Flory⁴. First evidence for this kind of mechanism

Scheme 1



resulted from the isolation of cyclobutane derivatives formed as by-products⁵. These cannot be produced in a synchronous reaction⁶ but rather *via* intermediates having biradical character. To give further evidence to this

hypothesis of a biradical acting as initiating species, additional experiments were performed to determine the reaction order referring to the monomer concentration of the initiation reaction by performing polymerizations in inert solvents. With this, the calculation of the activation parameters of the initiation step becomes possible.

Theoretical considerations lead to the conclusion that biradical growth to high polymers is not possible⁷. For this reason reaction paths had to be looked for, which avoid biradical growth, but still result in the formation of high polymers. As such transfer reactions are possible and can give rise to monoradicals not being subject to self-termination reactions such as biradicals are. An example of this kind of initiation mechanism is the role of THF in the polymerization photoinitiated by aromatic ketones⁸. Similar effects were described by Pryor *et al.* for the spontaneous polymerization of pentafluorostyrene⁹, for which the Mayo mechanism is not applicable, either. In both cases, however, a detailed analysis of the effect of different transfer agents in different concentrations has not been done.

Here we report the results of the kinetics of the spontaneous polymerization of MMA in a series of solvents of higher transfer power. To exclude effects other than those resulting from transfer reactions solvents having a broad variety of chemical structures were selected. Experiments in halogen-containing solvents, however, had to be excluded, since those obviously lead to a second path of participation in the initiation step, which will be treated in detail elsewhere (cf. Figure 2, ref. 10).

EXPERIMENTAL

Monomeric MMA, unstabilized, was supplied by Röhm, Darmstadt, and treated as described in part 1 of this

* Part of: J. Lingnau, Dissertation, University of Mainz, 1982.

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series^{2a}. Benzene, isobutyric acid methyl ester (IBME), 2-propanol (iPrOH), *N,N*-dimethyl-aniline (DMA), tri-*n*-butyl-amine (tBA), nitromethane (NM) and thiophenol (TP) were commercial products from Merck, Darmstadt. They were supplied in p.a. quality as far as possible. Solvent treatment followed the procedure described for monomer, i.e. the solvents were fractionated in a N₂ atmosphere twice over a silvermantle-column, whereby LiAlH₄ or CaH₂ was added in the cases of benzene or IBME, DMA, and tBA, respectively.

Since DMA is easily oxidized by molecular oxygen, it was subject to additional chromatography on Al₂O₃, while the other solvents were directly filled into the solvent stock flask of the high vacuum line used to fill the ampoules for the gravimetric runs^{2a}.

The solvents were then degassed by several freezing-thawing cycles and stored *in vacuo* until used.

The treatment of the ampoules and the filling procedure were performed as described earlier^{2a}. The composition of the solutions was additionally checked by g.c.

The kinetic runs were carried out at 130°C, 110°C and 90°C up to about 5% conversion. The reaction mixtures were diluted in acetone or chloroform and the polymer precipitated in methanol or petrol ether (40/80).

Molecular weights were determined by g.p.c. and viscometry.

KINETICS IN THE 'INERT' SOLVENT BENZENE

The results of the kinetic experiments in the kinetically 'inert'* solvent benzene are summarized in Table 1. A double logarithmic plot (Figure 1) of the overall rate of polymerization *versus* the monomer concentration gives a slope of 2.08, i.e. second order dependence of the rate on the monomer concentration. Therefore from the kinetic results of the bulk polymerization, the activation parameters of Table 2 may be obtained, which show a good agreement between the activation enthalpies of the initiation and cyclodimerization reactions and a value obtained from thermochemical calculations¹¹ for the formation of a dimeric tail-to-tail biradical $\cdot M_2\cdot$ from monomeric MMA. Thus energetic considerations support Pryor's biradical hypothesis.

KINETICS IN THE PRESENCE OF MORE EFFICIENT TRANSFER AGENTS

The addition of more efficient transfer agents leads to a rise of the overall polymerization rate, R_p , for small concentrations of the transfer agent [T], while for higher concentrations the rate decreases due to lower monomer concentrations (Figure 1). This behaviour may be understood by assuming transfer to the biradical according to Scheme 2.

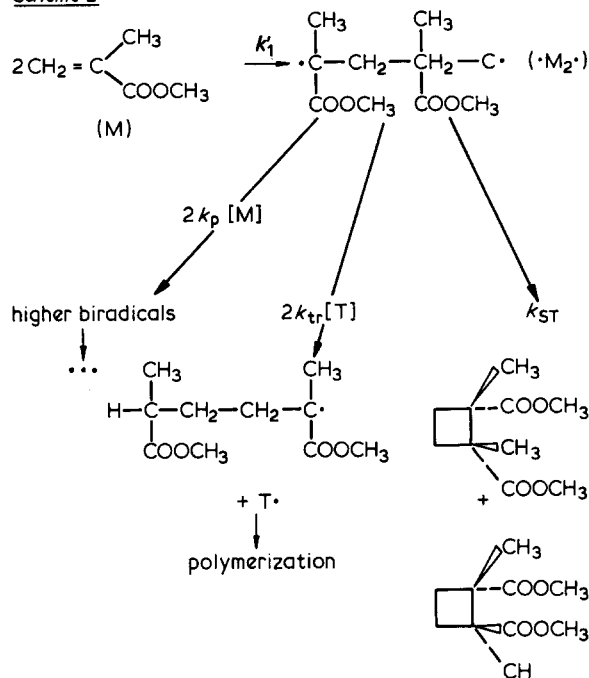
The balance of the concentration of the dimeric biradical $\cdot M_2\cdot$ is given by:

$$\frac{d[\cdot M_2\cdot]}{dt} = k'_1[M]^2 - \left(k_{ST} + \sum_T 2k_{tr}[T] + 2k_p[M] \right) [\cdot M_2\cdot] \quad (1)$$

$$\approx k'_1[M]^2 - k_{ST}[\cdot M_2\cdot] \quad (2)$$

* Benzene has a very low transfer constant, which may be neglected in a first approximation (cf. Table 3).

Scheme 2



where k_p , k_{tr} , k_{ST} , and k_t denote the rate constants of propagation, transfer to transfer agent, self termination, and termination, respectively.

In the steady state equation (2) yields:

$$[\cdot M_2\cdot] = \frac{k'_1}{k_{ST}} [M]^2 = k_1 [M]^2 \quad (3)$$

Biradicals of higher degree of polymerization may be neglected. The rate of initiation, R_i , according to Scheme 2 is given by:

$$R_i = \left(\frac{dP}{dt} \right)_{\text{form}} = \sum_T 2k_{tr}[T][\cdot M_2\cdot] + k_2[\cdot M_2\cdot] \quad (4)$$

where k_2 includes all other mechanisms leading to initiation. Thus for the overall rate of polymerization equations (5) and (6) result:

$$R_p = R_i^{1/2} \sqrt{\frac{k_p^2}{k_t}} [M] \quad (5)$$

$$R_p = \sqrt{\frac{k_p^2}{k_t}} [M]^2 k_1^{1/2} \sqrt{\left(k_2 + 2 \sum_T k_{tr}[T] \right)} \quad (6)$$

For the systems under consideration transfer to monomer may be neglected to a first approximation. Consequently a linearization should be possible by plotting $R_p^2/[M]^4$ *versus* solvent concentration.

A more detailed analysis leads to slight modification in the cases of rather weak transfer agents. Assuming 'transfer initiation' the system MMA/benzene yields a slope of 2.1 for $\log(R_p)$ *versus* $\log[M]$ using the transfer constants from Table 3.

Figure 2 shows a plot according to equation (6). The slopes in Figure 2 correlate directly with the transfer constants of the respective solvents (Figure 3). Thus the solvent effect on the spontaneous polymerization can be explained by the participation of a transfer step in the initiation process.

Table 1 Spontaneous polymerization of MMA in the presence of transfer agents. (a) Taken from J. Lingnau, Diplomarbeit, Mainz, 1978, (b) taken from ref. 11, (c) extrapolated from data given by Stickler, ref. 11. The values of k_t were corrected to the viscosity of the respective reaction media

Temperature	Solvent	Monomer concentration (mol l ⁻¹)	Solvent concentration (mol l ⁻¹)	$R_p \times 10^8$ (mol l ⁻¹ s ⁻¹)	$10^7 k_t$	$100 k_p^2/k_t$
130°C	Benzene	1.91	7.45	5.48	3.81	9.17
		5.29	3.40	44.00	3.81	9.17
		6.46	2.01	62.10	3.81	9.17
		2.54	3.60	9.22	3.81	9.17
		3.60	5.43	19.41	3.81	9.17
		1.10	8.41	1.27	3.81	9.17
		5.20	3.50	36.8	3.81	9.17
		3.67	5.28	17.2	3.81	9.17
		1.30	8.15	3.83	3.81	9.17
		130°C	IBME	3.83	3.96	11.00
6.13	1.84			44.73	3.84	9.11
2.50	5.18			11.03	3.89	9.00
1.23	6.35			2.57	3.91	8.95
5.16	2.75			71.05	3.85	9.08
6.87	1.17			98.81	3.83	9.14
130°C	iPrOH	3.02	7.23	35.0	3.77	9.28
		4.55	5.06	70.3	3.78	9.25
		1.24	9.77	5.96	3.75	9.33
		5.23	4.10	71.2	3.79	9.24
		6.47	2.36	106.0	3.80	9.21
130°C	DMA	8.00	0.10	140.0	3.75	9.31
		7.60	0.47	220.0	3.56	9.81
		3.24	4.29	40.0	2.37	14.78
		7.86	0.24	185.0	3.68	9.51
		7.29	0.74	162.0	3.44	10.17
130°C	tBA	7.95	0.12	75.8	3.74	9.34
		3.28	2.26	84.0	2.78	12.59
		7.90	0.15	132.4	3.73	9.39
		7.90	0.15	98.0	3.73	9.39
		7.02	0.55	96.1	3.51	9.95
		7.06	0.53	86.7	3.52	9.92
		7.98	0.11	92.3	3.75	9.33
		7.88	0.16	92.5	3.72	9.40
130°C	NM	7.40	1.72	274.0	3.71	9.43
		7.39	1.73	302.0	3.71	9.43
130°C	TP/C ₆ H ₆	4.74	1.54 × 10 ⁻² /4.06	401.0	3.81	9.17
		6.30	1.19 × 10 ⁻² /2.20	651.0	3.81	9.17
		2.28	3.77 × 10 ⁻² /7.01	129.0	3.81	9.17
		3.09	3.24 × 10 ⁻² /6.03	170.0	3.81	9.17
130°C	—	8.13 ^c	0.0	49.5	3.81	9.17
		8.13 ^c	0.0	52.0	3.81	9.17
		8.13 ^c	0.0	74.3	3.81	9.17
110°C	TP/C ₆ H ₆	3.66	3.04 × 10 ⁻² /5.65	71.6	3.51	5.27
		1.85	4.20 × 10 ⁻² /7.80	—	—	—
		6.18	1.42 × 10 ⁻² /2.63	152.4	3.49	5.30
110°C	Benzene	4.20 ^a	4.99	13.83	3.43	5.38
110°C	IBME	5.47 ^a	2.68	8.53	3.51	5.26
		7.31 ^a	0.98	58.25	3.49	5.31
110°C	—	8.38 ^a	0.0	37.3	3.47	5.33
90°C	TP/C ₆ H ₆	6.04	1.59 × 10 ⁻² /2.94	21.8	3.10	2.96
		3.41	3.35 × 10 ⁻² /6.22	10.0	3.06	3.00
90°C	—	8.62 ^c	0.0	5.44	3.14	2.92

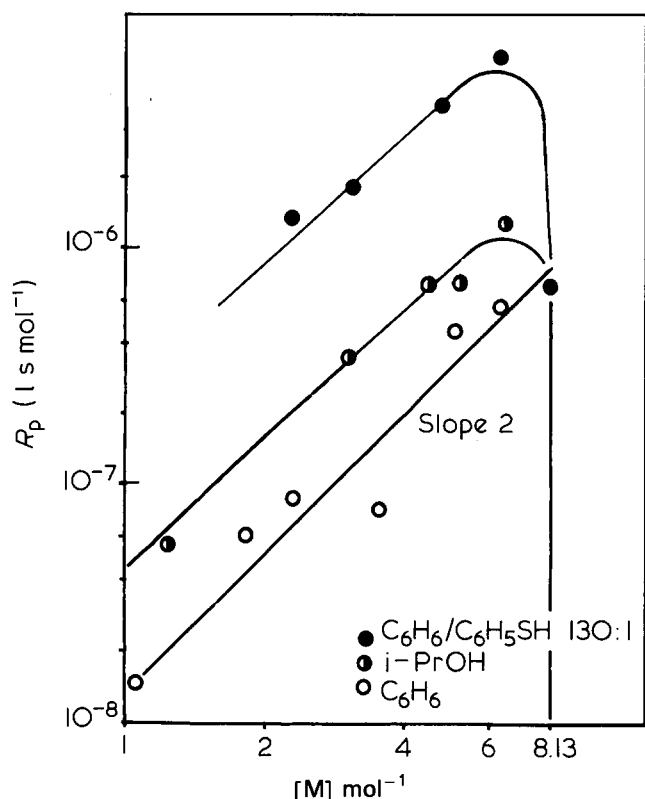


Figure 1 Kinetics of the spontaneous polymerization of MMA in the presence of transfer agents

Table 2 Activation parameters for oligomerization and initiation

Formation of	H (kJ mol ⁻¹)	S (J mol ⁻¹ K ⁻¹)	Reaction order
linear dimer	78	-183	2 in [M]
linear trimers	(80 88)	(-228 -190)	1 in [M] 1 in [H-1]
cis-cyclobutane	141	-102	2 in [M]
trans-cyclobutane	126	-140	2 in [M]
initiation in bulk	143	-178	2 in [M] (benzene)
dimer. biradical (thermochem. data)	142		

Table 3 Comparison between the transfer constants of the used solvents and their effect onto the spontaneous polymerization of MMA

Solvent	$C_s^{130} \times 10^4$	Slope of the plot $R_p^2 k_t / [M]^4 k_p^2$ vs. $[T] \times 10^{15}$
Benzene	0.12	≈ 0
MMA	0.67	≈ 0
IBME	1.49	0.39
iPrOH	2.04	1.89
DMA	18.5	5.7
tBA	33.4	5.7
NM	181	17.5
TP	42800	23000

The choice of solvents with higher transfer power excluding those containing halogen atoms is very limited. All solvents used have certain disadvantages which must be considered in more detail: Thiophenol, besides being toxic, contains sulphur which should exhibit a heavy atom effect comparable with that of neighbouring chlorine¹⁰.

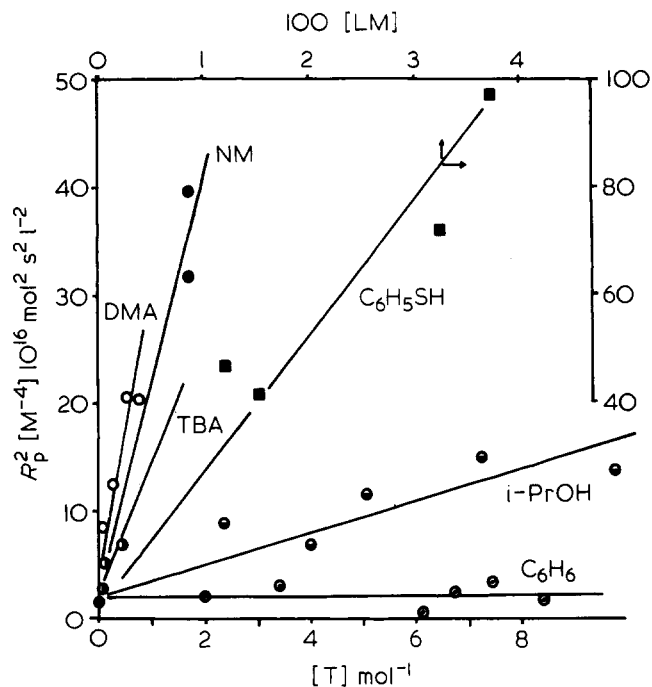


Figure 2 Linearization of the effect of transfer agents according to equation (2): \circ , benzene; \bullet , 2-propanol; \circ , *N,N*-dimethylaniline; \bullet , Tributylamine; \bullet , nitromethane; \blacksquare , thiophenol

The comparison of the contribution of thiophenol in acting as a transfer agent and in acting as a heavy atom containing solvent (this effect should be smaller than the heavy atom effect of CCl_4) shows that the latter should account for less than 0.5% of the acceleration.

Some authors¹²⁻¹⁴ claim that *N,N*-dimethylaniline is an effective initiator for the radical polymerization of MMA. Extrapolation of the data given by Tsuda *et al.*¹³ to 130°C gave a value $(k_i k_p^2 / k_t)^{1/2} = 4.3 \cdot 10^{-4}$ which is reasonably higher than the value $2 \cdot 10^{-7}$ found in the present work. This might be due to the fact that DMA is very easily oxidized by molecular oxygen¹⁵ and that DMA catalyses the absorption of oxygen by and the oxidation of acrylates¹⁴. These so formed peroxides are known to initiate the polymerization¹⁶. The good agreement between the results in DMA and other solvents shows that the initiation properties of DMA are limited to the participation in a transfer step as long as oxygen is entirely excluded from the reaction medium.

Nitromethane leads to weak retardation in the polymerization of MMA¹⁷ which may explain the deviation from a straight line in Figure 3.

Tributylamine and Isopropanol are precipitating agents for PMMA, thus limiting their experimental concentration range. At the same time kinetics may deviate from ideality¹⁸.

All these effects, however, are small as compared with the 'transfer effect' discussed in the present work and do not lead to serious alterations in Figure 3.

TEMPERATURE DEPENDENCE OF THE EFFECT OF TRANSFER AGENTS ON THE INITIATION OF THE SPONTANEOUS POLYMERIZATION OF MMA

Additional proof for the context between the transfer power of solvents and their effect on the spontaneous polymerization results from the temperature dependence of

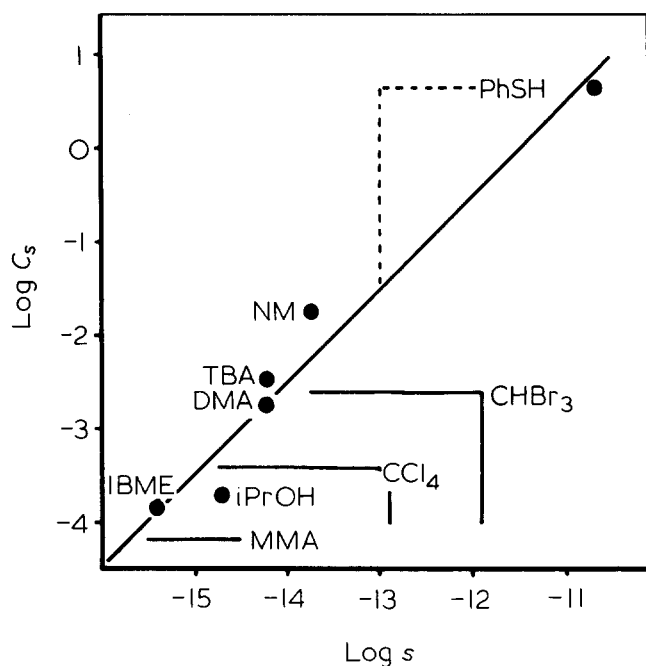


Figure 3 Dependence of the effect of transfer agents on the initiation step on the transfer constant. Values refer to 130°C. Values for CCl₄ and CHBr₃ are given for comparison (see text). $C_s = k_{tr}/k_p$; $s = \text{slope of } R_p^2 k_t / k_p^2 [M]^4 \text{ vs. } [T]$

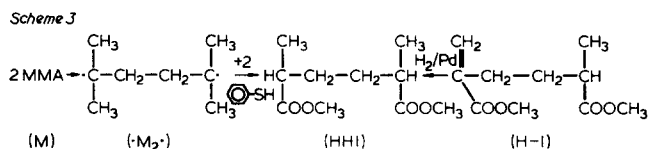
both. Table 4 gives the results obtained at different temperatures from samples containing thiophenol, benzene, and MMA. Assuming $k_2 \ll 2k_{tr}[T]$ and $1/P_n \approx k_{tr}[T]/k_p[M]$ equation (6) yields:

$$\frac{R_p^2 k_t}{k_1 k_p^3} = \frac{2[M]^5}{P_n}$$

(the experimental error in the determination of P_n is smaller than in the determination of $[T]$). Figure 4 shows that in fact one straight line is obtained which is independent of temperature. The value of the slope is somewhat below 2, probably due to slight retardation.

SCAVENGING OF BIRADICAL $\cdot M_2$

The above results and considerations directly lead to a simple proof for the existence of the dimeric biradical $\cdot M_2$ as an intermediate of the initiation mechanism for the spontaneous polymerization of MMA. An increase in the concentration of a strong transfer agent should yield a detectable amount of double transferred HHI, a compound which is easily accessible as a reference compound by hydrogenation of the linear dimer H-1 (see ref. 2b):



To suppress a strong decline of the monomer and thiophenol concentrations by reactions other than the initiation reaction, benzoquinone was added in this trapping experiment. Figure 5 shows the g.c.-mass spectrum obtained from a reaction mixture of MMA:thio-

Table 4 Temperature dependence of the transfer effect of thiophenol

Temperature (°C)	C_{TP}	Slope of the plot $R_p^2 k_t / [M]^4 k_p^2$ vs. $[TP]$
130	4.28	2.30×10^{-11}
110	2.78	1.91×10^{-12}
90	2.05	7.8×10^{-14}

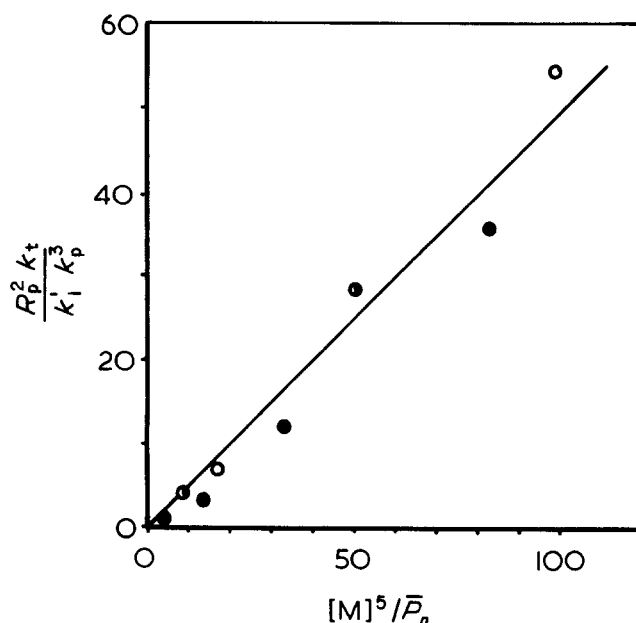


Figure 4 Plot to demonstrate the equivalent temperature dependence of both the transfer constants and the acceleration of the spontaneous polymerization according to equation (3): ●, 130°C; ○, 110°C; ◐, 90°C

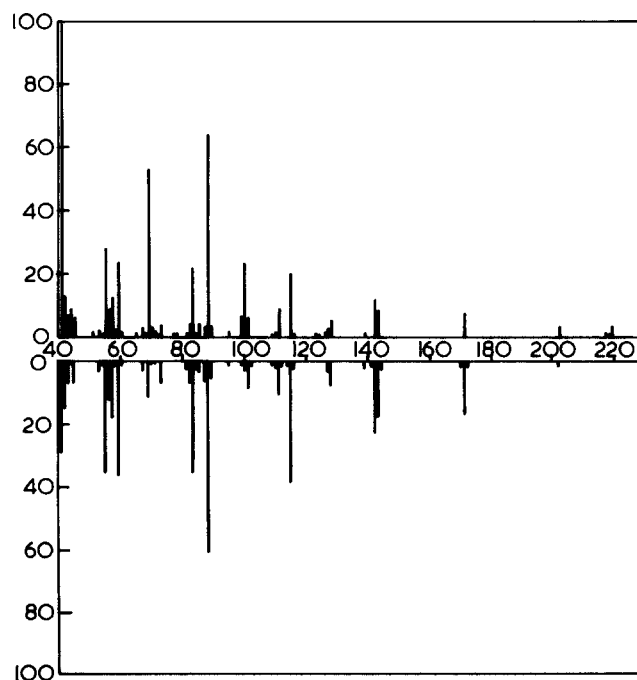


Figure 5 Mass spectra of double transferred product HHI. (a): from g.c.-MS coupling, reaction mixture cf. text. (b) reference obtained by hydrogenation of H-1

phenol:benzoquinone 5 ml:2 ml:500 mg after 400 h at 130°C together with the mass spectrum of the reference compound HH1. The M^+ peak at 202 and the agreement in the peak pattern clearly demonstrate the identity of both compounds, and thus give direct evidence for the biradical $\cdot M_2\cdot$. (Other peaks could be assigned to monomer, thiophenol, and the monomer-thiophenol adduct.)

CONCLUSIONS

A conclusion that may be drawn from the experimental results presented here is that a biradical $\cdot M_2\cdot$ must be seen as being the central compound in the initiation mechanism of the spontaneous polymerization of MMA. The reaction sequence, including initiation *via* a transfer step as given in *Scheme 2*, is able to explain the effect of different solvents on the spontaneous polymerization of MMA at various temperatures. Biradical growth, though not impossible but rather improbable, yields biradicals of higher degrees of polymerization with a corresponding multiplicity of reactions. Their contribution to the initiation may be neglected, especially since the self-termination reaction of $\cdot M_3\cdot$, yielding a six-membered ring system, should dominate even more over transfer and growth reactions. Biradical growth to high polymers by this mechanism can consequently be ruled out.

Additional experimental work on the spontaneous polymerization of MMA in halogen containing solvents and of substituted methacrylates, however, leads us to the conclusion that *Scheme 2* reveals just one pathway of the complete initiation mechanism. Details of this work will be published in forthcoming papers.

ACKNOWLEDGEMENT

Support of this work by the 'Deutsche Forschungsgemeinschaft' through the Sonderforschungsbereich 41 and by a stipend of the 'Studienstiftung des Deutschen Volkes' (J.L.) is gratefully acknowledged.

REFERENCES

- 1 Pryor, W. A. and Lasswell, L. D. 'Advances in Free Radical Chemistry', Vol. V, Academic Press, New York, 1975
- 2 (a) Stickler, M. and Meyerhoff, G. *Makromol. Chem.* 1978, **179**, 2729; (b) Stickler, M. and Meyerhoff, G. *Makromol. Chem.* 1980, **181**, 131; (c) Brand, E., Stickler, M. and Meyerhoff, G. *Makromol. Chem.* 1980, **181**, 913; (d) Stickler, M. and Meyerhoff, G. *Polymer*, 1981, **22**, 928
- 3 Mayo, F. R. *J. Am. Chem. Soc.* 1968, **90**, 1289
- 4 Flory, P. J. *J. Am. Chem. Soc.* 1937, **59**, 241
- 5 Lingnau, J., Stickler, M. and Meyerhoff, G. *Eur. Polym. J.* 1980, **16**, 785
- 6 Woodward, R. B. and Hoffmann, R. *Angew. Chem.* 1969, **81**, 797; Wright, J. S. and Salem, L. *J. Am. Chem. Soc.* 1972, **94**, 322; Coks, A. T., Frey, H. M. and Stevens, D. R. *Chem. Comm.* 1969, 458; Baldwin, J. E. and Ford, P. W. *J. Am. Chem. Soc.* 1969, **91**, 7192
- 7 Haward, R. N. *Trans. Faraday Soc.* 1950, **46**, 204; Zimm, B. H. and Bragg, J. K. *J. Polym. Sci.* 1952, **9**, 476
- 8 Block, H., Ledwith, A. and Taylor, A. R. *Polymer* 1971, **12**, 271; Ledwith, A., Ndaalio, G. and Taylor, A. R. *Macromolecules* 1975, **8**, 1; Merlin, A., Lougnot, D. J. and Fouassier, J. P. *Polym. Bull.* 1980, **2**, 847; McGinniss, V. D., Provder, T., Kuo, C. and Gallapo, A. *Macromolecules* 1978, **11**, 393; McGinniss, V. D. and Dusek, D. M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1974, **15**, 480; Granchak, V. M., Kondratenko, P. A., Sherstynk, V. P. and Dilung, I. I. *Vysokomol. Soedin.* 1980, **22A**, 2045
- 9 Pryor, W. A., Iino, M. and Newkome, G. R. *J. Am. Chem. Soc.* 1977, **99**, 6003
- 10 Lingnau, J. and Meyerhoff, G. *Macromolecules*, in press
- 11 Stickler, M. Dissertation, Mainz, 1977
- 12 Chao, W. H., Li, C. H., Fung, H. T. and K'o Hsueh T'ung Pao 1980, **25**, 730 (C.A. 93; 205.107g)
- 13 Ishida, T., Kondo, S. and Tsuda, K. *Makromol. Chem.* 1977, **178**, 3221
- 14 Chao, W. H., Fung, H. T. and K'o Hsueh T'ung Pao 1980, **25**, 310 (C.A. 93:26.885h)
- 15 Bakhturidze, G. Sh., Aleksandrov, A. L. and Edilashvili, I. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1979, 515
- 16 Matsumoto, T., Mune, I. and Sigemasa, Y. *Kobunshi Kagaku* 1969, **286**, 180
- 17 Shreibert, A. I., Khradin, A. P., Tishkov, P. O., Propkop'ev, P. and Shestakova, A. D. *Vysokomol. Soedin* 1967, **89**, 517
- 18 Noma, K., Tajima, Y. and Niwa, M. *Sci. Eng. Revs. Doshisha Univ. Kyoto* 1962, **3**, 427; Barton, J., Capek, J. and Juranicova, V. *Chem. Zvesti* 1979, **33**, 774