

NOTE

Thermal Radical Polymerization Reactions with Polystyrene and Poly(methyl methacrylate) Macroinitiators Containing Thiyl End-Groups

INTRODUCTION

The course of the radical polymerization and the properties of the polymers formed depend greatly on the means of initiation of the polymerization process. When using iniferters, i.e., initiators that are efficient chain transfer agents and are characterized by facile reversible primary termination of the radicals formed by their decomposition, monofunctional or α,ω -bifunctional polymers are obtained.¹ These can mediate in the extension of the polymer chain or synthesis of block copolymers. Following dissociation of the reversibly terminated polymers to polymer radicals and iniferter fragments, further growth reactions with the monomer present can occur on the chains.¹⁻⁵

Iniferters facilitating the formation of monofunctional polymers include, e.g., phenylazo(triphenylmethane), *S*-(phenylazo)thiophenol, 1,3-diphenyltriazene, and organic monosulfides; organic disulfides, tetraalkyl tetrazenes, and polyhalogen alkanes have been found useful for the preparation of α,ω -bifunctional polymers.¹ A considerable amount of attention has been paid, especially to organic disulfides used in photochemical polymerization.^{1,3-5} For example, under the conditions of photoinitiated radical polymerization or copolymerization of styrene and methyl methacrylate in the presence of tetraethylthiuram disulfide, the corresponding telechelic polymers were first prepared with thiyl end-groups (macroinitiators); they were used to synthesize both homopolymers with higher molecular weights and block copolymers.^{1,5}

This study deals with the thermal radical polymerization of styrene and methyl methacrylate initiated by their macroinitiators with diethyl thiocarbamoylthio end-groups. A description is given of the preparation and properties of the same types of polymer products as are formed in the presence of these macroinitiators in photopolymerization.

EXPERIMENTAL

Styrene (S) (b.p. 36°C/1.56 kPa), methyl methacrylate (MMA) (b.p. 42°C/10.4 kPa) and 2,2'-azobis(isobu-

tyronitrile) (AIBN) (m.p. 105°C) were first purified by the procedure described earlier.⁶ Tetraethylthiuram disulfide (TDS) (m.p. 71°C) was prepared by oxidation of *N,N*-diethyldithiocarbamate.⁷

The polymerization reactions were carried out in sealed glass ampoules in a nitrogen atmosphere at 50–80°C. The polymers were precipitated from the reaction mixture and reprecipitated with methanol after dissolving in benzene. After drying in vacuum, the limiting viscosity numbers were determined for the styrene polymers (PS) in benzene at 25°C and for the methyl methacrylate polymers (PMMA) in benzene at 30°C. The average molecular weights (n) were calculated from the equations:

$$[\eta] = 4.37 \times 10^{-4} \times \bar{M}_n^{0.66} \quad (\text{for PS})^8$$

$$[\eta] = 6.27 \times 10^{-5} \times \bar{M}_n^{0.76} \quad (\text{for PMMA})^9$$

The polystyrene-equivalent molecular weights of the block copolymers were determined by the GPC method with tetrahydrofuran as eluent.

RESULTS AND DISCUSSION

Polystyrene and Poly(methyl methacrylate) Macroinitiators with Thiyl End-Groups

Polystyrene and poly(methyl methacrylate) macroinitiators (M-S and M-MMA, respectively) (Table I) were prepared in two ways: (a) by radical polymerization of S or MMA in a benzene solution initiated by AIBN in the presence of iniferter TDS, or (b) by radical polymerization of monomers in the presence of solvents initiated by iniferter TDS alone.¹ In the use of AIBN together with TDS, the polymer chains were terminated by both isobutyronitrile and thiyl groups,¹⁰ while in polymerization with TDS alone, two thiyl end-groups were present for each polymer molecule.¹ The molecular weight of the macroinitiators obtained did not exceed 45,000.

Table I Polymerization of Styrene and Methyl Methacrylate with Tetraethylthiuram Disulfide (TDS) as Iniferter

No.	Monomer (g)	TDS (g)	AIBN (g)	Benzene (mL)	Yield (%)	$\bar{M}_n \times 10^{-4}$
1	S (10.0)	0.2817	0.0821	14.3	12.6 ^a	1.2 ^b
2 ^c	S (28.1)	0.4500	—	—	39.0	4.2
3	MMA (5.0)	0.2966	0.1642	40.0	10.0 ^d	4.5 ^e
4 ^c	MMA (10.0)	0.2500	—	—	18.0	3.9

^a 50°C, 16 h.^b Viscometrically in benzene at 25°C using the relation $[\eta] = 4.37 \times 10^{-4} \times \bar{M}_n^{0.66}$.^c Ref. 2.^d 50°C, 6 h.^e Viscometrically in benzene at 30°C using the relationship $[\eta] = 6.27 \times 10^{-5} \times \bar{M}_n^{0.76}$.**Polymerization with Polystyrene or Poly(methyl methacrylate) Macroinitiators**

The results of the thermal radical polymerization initiated by polystyrene and poly(methyl methacrylate) macroinitiators are summarized in Table II. Heating of styrene at 80°C with M-S macroinitiator obtained by the polymerization of styrene in the presence of AIBN and TDS led to a product with an amount and molecular weight that were several times larger than that of the initial M-S. Also, the amount and in particular the molecular weight of poly(methyl methacrylate) prepared from the M-MMA macroinitiator and MMA convincingly proved that the chain of the initial macroinitiator was extended.

The heating of the monomer alone to 80°C for 5 h did not lead to thermal polymerization of methyl methacrylate, while the observed conversion of styrene correspon-

ded to about 2.4%. The product obtained from the M-S macroinitiator and styrene could thus also contain, in addition to polystyrene with a prolonged chain, PS from the thermal polymerization of styrene, which occurred without an initiator, and unreacted M-S. The products from polymerization of MMA initiated by M-MMA contained poly(methyl methacrylate) with a prolonged chain and unreacted M-MMA.

It is apparent from the amount of polymers obtained by heating the macroinitiator of styrene and monomeric methyl methacrylate that the isolated product contained the block copolymer PS-PMMA. Similarly, it can be concluded that the PMMA-PS copolymer is formed, based on the amount of product isolated after heating the M-MMA macroinitiator with styrene. The amount of homopolymers accompanying the final block copolymers was found using selective extraction methods.⁵ Polystyrene was

Table II Polymerization of Styrene and Methyl Methacrylate with Polystyrene or Poly(methyl methacrylate) Macroinitiators (M-S or M-MMA) (5 mL of Monomer, 80°C, 5 h)

Macroinitiator (g)	Monomer	Polymer Obtained ^a (g)	PS (wt % of Homopolymer)		PMMA	$\bar{M}_n \times 10^{-4}$ (b)
M-S ^c (0.30)	S	PS (0.75)	100	0	0	6.1
M-S ^c (0.30)	MMA	PS-PMMA (2.50)	1.9	0	0	5.2
M-S ^d (0.30)	MMA	PS-PMMA (1.04)	1.6	0	0	8.3
M-S ^d (0.30)	MMA	PS-PMMA (1.01) ^e	1.6	0	0	7.4
M-MMA ^f (0.22)	S	PMMA-PS (0.46)	19.6	54.4	54.4	34.8
M-MMA ^f (0.30)	MMA	PMMA (0.87)	0	100	100	54.7
M-S ^d (0.30)	§	PS (0.30) ^h	100	0	0	4.2
—	S	PS (0.11)	100	0	0	—
—	MMA	—	0	0	0	—

^a Including unreacted macroinitiator.^b \bar{M}_n values of homopolymers and block copolymers were determined viscometrically and by GPC, respectively (Table I).^c From experiment No. 1 (Table I).^d From experiment No. 2 (Table I).^e Polymerization temperature 60°C.^f From experiment No. 3 (Table I).[§] 2 mL of benzene.^h Polymerization temperature 60°C, reaction time 20 h.

transferred to the cyclohexane extract (extraction at room temperature for 24 h); poly(methyl methacrylate) was removed by extraction with acetonitrile (room temperature, 20 h) and ethanol (40°C, 5 h). For PS-PMMA, 1.6–1.9% of unreacted macroinitiator was found; addition of MMA to the macroinitiator chain containing only thiyl end-groups occurred with a lower yield than when using M-S with thiyl and isobutyronitrile end-groups, where there were probably fewer transfer and terminal reactions, retarding propagation. As expected, the molecular weight was higher in the case of the addition of MMA to the polystyrene biradicals from M-S with two thiyl groups in the polymer chain. The product obtained in the polymerization of styrene initiated by the poly(methyl methacrylate) macroinitiator contained more than 50% of the initial M-MMA and about 20% polystyrene. The molecular weight of the PMMA-PS block copolymer was severalfold larger than that of the PS-PMMA copolymer. This indicates that, in the formation of the block copolymers, styrene, in contrast to MMA, adds to a much smaller number of polymer radicals from the macroinitiator. On the basis of this finding, the synthesis of the block PS-PMMA copolymers proceeds with greater initiation efficiency and yields a purer product than the synthesis of PMMA-PS.

Otsu et al. found that the photolysis of polystyrene or poly(methyl methacrylate) containing thiyl end-groups at 30°C leads to the formation of polymers with higher molecular weights, while after heating to 80°C in benzene molecular weights of the initial macroinitiators and isolated polymers were the same.¹ Thus, further research on macroinitiators with thiyl groups was concerned exclusively with study of their roles in photopolymerization processes. However, our results confirmed that polymers with prolonged chains and block copolymers can be prepared not only through photopolymerization, but also by thermal polymerization with macroinitiators containing thiyl end-groups. Comparison of the different behavior of macroinitiators during heating in benzene and during irradiation with UV light is apparently connected with the effect of temperature on the polymerization process. Under photolysis conditions at 30°C, dissociation of the thiyl group could be followed not only by growth reactions in the presence of the monomer, but also by recombination of the polymer radicals from the initial macroinitiator. However, at higher temperatures the polymer radicals from the initial macroinitiator apparently readily enter into a termination reaction with the dissociated iniferter fragments or add the monomer present, and their recombination does not occur.

The absence of PMMA (homopolymer) in the thermal polymerization using the system polystyrene macroinitiator-methyl methacrylate (Table II) obviously has also a close relation with termination reactions at a higher temperature. Contrary to the photochemically initiated polymerization,^{11,12} in the thermal polymerization the growing polymer radicals can be largely terminated by thiyl radicals from the dissociated M-S and,

consequently, the thiyl radicals do not initiate the homopolymerization of MMA.

The effect of temperature on the process of the thermal polymerization with macroinitiators with thiyl groups is also apparent from the data in Table II, giving the amounts of products obtained by heating the polystyrene macroinitiator with MMA at 80 and 60°C. These were practically the same in both cases, more than three times larger than the amount of initial macroinitiator. Because of the determination of the same amount of unreacted macroinitiator, it can be assumed a higher initiation efficiency at 60°C and higher participation of the degradative chain transfer by the macroinitiator at 80°C with retardation of the propagation reaction. The lower molecular weight found for the block copolymer prepared at 60°C is in agreement with the expected higher initiation efficiency of M-S at this temperature. However, similarly to a temperature of 80°C, at 60°C polystyrene with higher molecular weight is not formed from the M-S macroinitiator alone, i.e., even at 60°C bimolecular recombination of the polymer radicals from the macroinitiator does not occur.

The process of the solution polymerization was studied by heating polystyrene macroinitiator (0.30 g) with MMA (2.5 mL) for 5 h at 60°C in the presence of benzene (2.5 mL). The amount of isolated product was only 40% higher compared with the initial M-S.

The observed effect of the polymerization temperature and solvent added can be used to regulate the studied polymerization reactions.

CONCLUSION

Thermal polymerization of styrene or methyl methacrylate with macroinitiators derived from these monomers and containing thiyl end-groups was used to prepare PS and PMMA homopolymers with prolonged chains and block copolymers. Compared with the synthesis of the block copolymers initiated by poly(methyl methacrylate) macroinitiators, the synthesis initiated by polystyrene macroinitiators occurred with higher initiation efficiency and the products obtained contained only a small amount of unreacted macroinitiator. Polymerization and the formation of the products can be affected by the polymerization temperature and solvent added.

This study was supported by Kaučuk Group, a.s., 278 52 Kralupy, Czech Republic.

REFERENCES

1. T. Otsu and M. Yoshida, *Makromol. Chem., Rapid Commun.*, **3**, 127 (1982).
2. T. Otsu, M. Yoshida, and T. Tazaki, *Makromol. Chem., Rapid Commun.*, **3**, 133 (1982).
3. P. Lambrinos, M. Tardi, A. Polton, and P. Sigwalt, *Eur. Polym. J.*, **26**, 1125 (1990).

4. S. Gaynor, D. Greszta, D. Mardare, M. Teodorescu, and K. Matyjaszewski, *J. Macromol. Chem.*, **A 31**, 1561 (1994).
5. M. Opresnik and A. Šebenik, *Polym. Int.*, **36**, 13 (1995).
6. J. Lokaj and F. Hrabák, *Angew. Makromol. Chem.*, **67**, 1 (1978).
7. R. Rothstein and K. Binovic, *Rec. Trav. Chim.*, **73**, 561 (1954).
8. D. C. Pepper, *J. Polym. Sci.*, **7**, 347 (1951).
9. T. G. Fox, J. B. Kinsinger, H. F. Mason, and E. M. Schneck, *Polymer*, **3**, 71 (1962).
10. T. Otsu and T. Naytani, *Makromol. Chem.*, **27**, 142 (1958).
11. T. Otsu and A. Kuriyama, *Polym. Bull.*, **11**, 135 (1984).
12. R. Turner and R. W. Blevins, *Macromolecules*, **23**, 1856 (1990).

J. LOKAJ^{1,*}
K. BOUCHAL¹
D. KONEČNÝ²

¹Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
162 06 Prague 6, Czech Republic
²Kaučuk Group, a.s.,
278 52 Kralupy, Czech Republic

Received March 18, 1996

Accepted June 27, 1996

* To whom correspondence should be addressed.