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Radical polymerization of methyl methacrylate with some 1,2-disubstituted tetraphenylethanes as thermal iniferters

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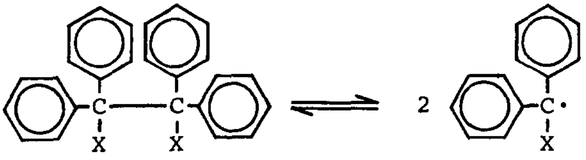
SUMMARY

The bulk polymerization of methyl methacrylate (MMA) with 1,2-disubstituted tetraphenylethanes, tetraphenylsuccinodinitrile (TPSN), tetra(p-methoxyphenyl)succinodinitrile (TMPSN), and pentaphenylethane (PPE), was investigated. These compounds were found to serve as thermal iniferters to induce living radical polymerization via a mechanism close to the model proposed previously (see Eq. 2). However, the living nature was not so high, because undesirable side reactions occurred. The oligomer with molecular weight of 2500 was isolated from the reaction mixture of MMA with TPSN, which was found to cause further polymerization of MMA. From the polymerization of styrene (St) with the polymers obtained by these iniferters, the block copolymers were produced.

INTRODUCTION

In 1900, Gomberg [1,2] reported that hexaphenylethane (1, X= C_6H_5) exists as an equilibrium mixture with triphenylmethyl radicals (2, X= C_6H_5). Since this discovery, the synthesis, characterization and reactions of 1 (or 2) and its derivatives have been investigated by many chemists. These radicals like 2 are so stable and do not initiate vinyl polymerization, but they easily react with radicals to form stable compounds.

In 1939, Schulz and coworkers [3-5] found, however, that TPSN (1,2-dicyanotetraphenylethane) (1, X= CN), an analogue of hexaphenylethane (1, X= C_6H_5), can serve as a radical initiator. Although the radical 2 (X= CN) is not so reactive for initiation, some 1,2-disubstituted tetraphenylethanes were thereafter synthesized by several workers [6-11] and tested as radical initiators (Eq. 1). Especially, Braun and coworkers [8-11] recently investigated the oligomerization of MMA with some 1,2-disubstituted tetraphenylethanes:

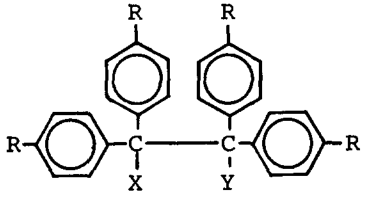


1 2 (1)

in where X is CN [3-5], C_2H_5, $-(CH_2)_3-$ [6,7], OC_6H_5 [8-10], and $OSi(CH_3)_3$ [11].

In 1981, we reported a concept of iniferter technique for novel polymer synthesis and design through radical polymerization [12]. Simultaneously, we proposed the model for living radical polymerization in a homogeneous system by the use of some iniferters [13]. Among the iniferters used, N,N-diethyldithiocarbamate derivatives and phenylazotriphenylmethane were found to be excellent photo- and thermal iniferters, respectively, to induce living radical polymerization via a mechanism close to this model [13-22]. The oligomerization of MMA with 1 (X= OC_6H_5) reported by Braun and coworkers [8-10] also seemed to resemble to this model. Recently, we reported briefly that TPSN induced living radical polymerization of MMA [23].

To clarify further the mechanism of the polymerization of MMA with 1,2-disubstituted tetraphenylethanes, the following derivatives were synthesized and used as thermal iniferters of the polymerization of MMA. The results obtained are described in this paper.



TPSN: R = H, X = Y = CN

TMPSN: R = OCH_3, X = Y = CN

PPE: R = H, X = H, Y = C_6H_5

EXPERIMENTAL

TPSN was synthesized by oxidative coupling of diphenylacetonitrile with iodine, and purified by recrystallization from anisole [24,25]: mp 222-223°C (lit.[24,25] 223-224°C). ^{13}C-NMR($CDCl_3$): δ = 58.1, 121.0, 127.9, 128.4, 130.0, 136.9 ppm. TMPSN was prepared by oxidative coupling of di(p-methoxyphenyl)acetonitrile, which was obtained from the condensation of anisaldehyde cyanhydrin with anisole, with potassium ferrocyanide [26,27], and then recrystallized from pyridine: mp 218-220°C (lit.[27] 220-240°C). ^{13}C-NMR($CDCl_3$): δ = 55.5, 58.6, 113.4, 121.6, 129.5, 131.4, 159.5 ppm. PPE was obtained by the reaction of triphenylmethylmagnesium bromide with diphenylmethyl chloride and recrystallized from a mixture of chloroform and methanol [28]: mp 165-172°C (lit.[28] 166-178°C). ^{13}C-NMR($CDCl_3$): δ = 59.5, 62.8, 126.0, 127.0, 127.5, 131.5, 131.8, 143.1, 145.8 ppm.

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. MMA and St were used after distillation under reduced pressure before use. Solvents and precipitants were used after purification according to ordinary methods.

Polymerization was carried out in a degassed sealed glass tube with shaking in a thermostat maintained at a given temperature. After polymerization, the content of the tubes was poured into a large amount of methanol to precipitate the polymer. The oligomer was isolated by pouring the polymerization mixture into excess n-hexane. The polymer yield was determined from the weight of the dried polymer. To know the oligomer formation during the polymerization, direct gel permeation chromatography (GPC) measurement of the polymerization mixture was carried out as a function of reaction time.

Block copolymerization was also performed with similar manner. Separation of block polymers from polymer mixtures obtained was carried out by extracting with a suitable solvent, i.e. acetonitrile, cyclohexane, and benzene for homopoly(MMA), homopoly(St), and block copolymer, respectively.

Intrinsic viscosity, $[\eta]$, of the poly(MMA)s was determined in benzene at 30 °C, and their average molecular weights ($\bar{M}$) were calculated from the equation [29].

$$[\eta] = 5.2 \times 10^{-5}\ \bar{M}^{0.76}$$

GPC was performed with tetrahydrofuran as an eluent at 38 °C by a Toyosoda CCPD, RE-8000, RI-8000, and UV-8000 equipped with columns: G-6000H, G-4000H, G-4000H, and G-2000H. ^{1}H- and ^{13}C-NMR spectra were measured by using JEOL JNM PS-100 and JEOL PFT-FX60Q spectrometers in deuterochloroform in the presence of tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

The results of bulk polymerization of MMA with TPSN, TMPSN, and PPE as initiators are summarized in Table 1, in which those with AIBN are also included.

As can be seen from this table, these tetraphenylethanes hardly induce radical polymerization in comparison with AIBN. Since the solubility of TMPSN in MMA was too low, the polymerization activity of these initiators could not be compared directly, but it seemed to be in the order: PPE > TMPSN > TPSN. PPE gave a low $\bar{M}$ polymer rather than TPSN and TMPSN, indicating that the radical 2 (X= C_6H_5) is more reactive for primary radical termination (PRT) than the radical 2 (X= CN). Moreover, TPSN was observed to act as a weak initiator for the polymerization of St, whereas it served as an inhibitor for vinyl acetate and vinyl chloride. These results seem to be accounted for by the fact that 2 (X= CN), whose unpaired

Table 1 Results of Bulk Polymerization of MMA with TPSN, TMPSN, PPE and AIBN

Initiator[a]	Temp. (°C)	Time (hr)	Yield[b] (%)	$\bar{M} \times 10^{-4}$
TPSN	60	20	7.2	211
	70	10	10.1	177
TMPSN	60	20	4.3	188[c]
	70	10	5.3	165[c]
PPE	60	20	15.5	8.2
	70	10	15.6	6.9
AIBN	60	5	29.6	280
	70	0.8	17.8	40.3

a) [Initiator] = 1.0×10^{-2} mol/L, except [TMPSN] = 5.0×10^{-4} mol/L, [AIBN] (60 °C) = 1.0×10^{-3} mol/L. b) The polymers polymers were isolated by precipitating with methanol. c) Weight-average molecular weight by GPC.

electron is delocalized through the substituents, can react with more-reactive conjugative monomers to initiate polymerization, but for non-conjugative monomers, it functions as a terminator rather than an initiator. Anyhow, since these tetraphenylethanes can serve both initiator and terminator for MMA, they are expected to act as thermal iniferters.

To confirm further this point, the bulk polymerization of MMA with various concentrations of TPSN was attempted at 70 °C. The results are shown in Figure 1. When the concentration of TPSN increased more than 1 x 10^{-3} mol/L, an induction period, which increased with its concentration, appeared, although the rates of polymerization after induction period increased linearly with the TPSN concentration. From the slope of this straight line, the order of the rate with respect to the TPSN concentration was confirmed to be 0.3, indicating

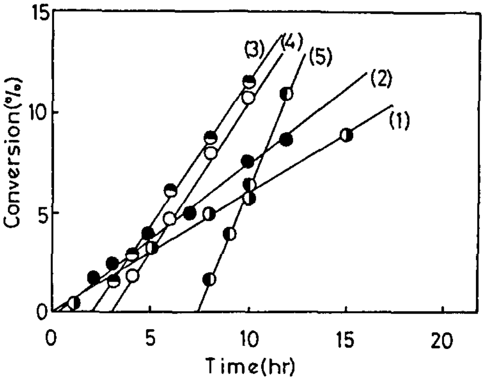


Figure 1 Time-conversion relations for bulk polymerization of MMA with TPSN at 70°C:[TPSN] = 0.05(1); 0.1(2); 0.5(3); 1.0(4); 5.0 x 10^{-2} mol/L(5).

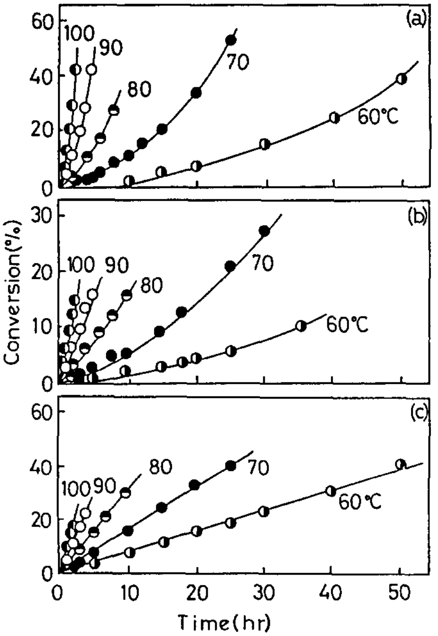


Figure 2 Time-conversion relations for bulk polymerization of MMA with TPSN(a), TMPSN(b), PPE(c): [TPSN]=[PPE]= 1.0 x 10^{-2} mol/L, [TMPSN]= 5.0 x 10^{-4} mol/L.

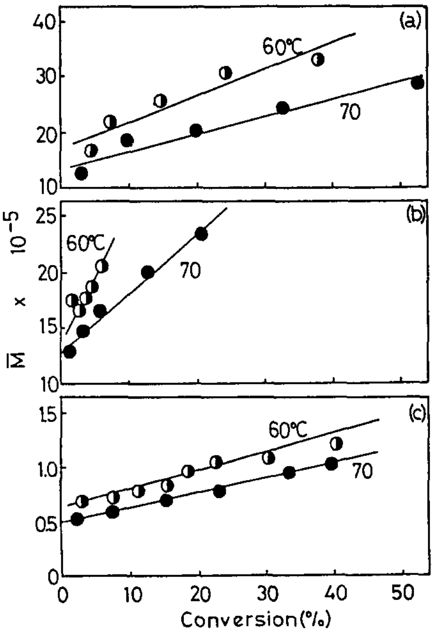
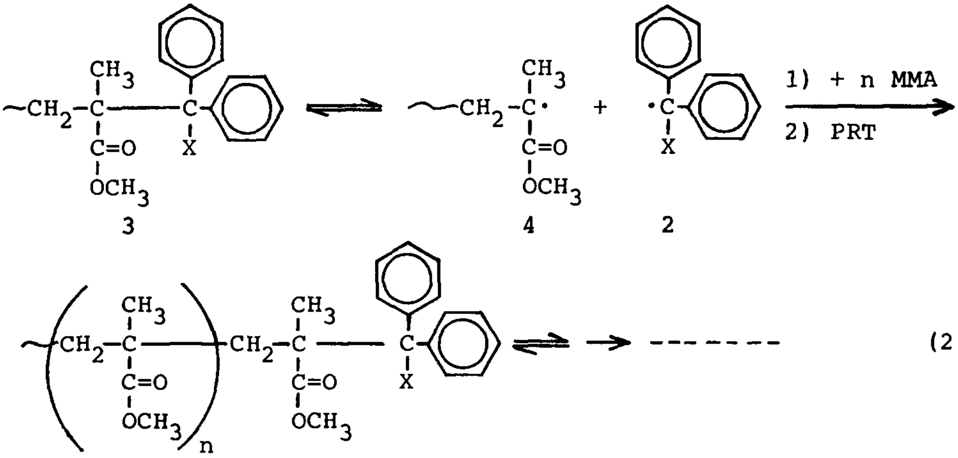


Figure 3 Conversion-$\overline{M}$ relations with TPSN(a),TMPSN(b),PPE(c); conditions see Figure 2.

that primary radical termination played an important role in this polymerization. Similarly, the addition of TPSN to the polymerization of MMA with AIBN at 70 °C gave some induction periods and decreased the polymerization rate. During induction period, the formation of the oligomer was observed (see the later part).

The time-conversion relations of bulk polymerization of MMA with TPSN, TMPSN and PPE at various temperatures are shown in Figure 2. In these relations obtained by TPSN and TMPSN, induction period and autoacceleration effect were also observed when the polymerization temperature decreased.

Figure 3 shows conversion-$\bar{M}$ relations for these polymerizations at 60 and 70 °C. As seen from this figure, the $\bar{M}$ of the polymers increased with conversion, i.e. reaction time. Similar results were also found for bulk polymerization of MMA with 1 (X= C_2H_5, $-(CH_2)_3-$ [6,7] and CN [3-5,11]), and for the oligomerization of MMA with 1 (X= OC_6H_5 and CN [8-11]). Such findings are taken to indicate that these tetraphenylethanes serve as iniferters and induce a living radical polymerization according to the model (Eq. 2) reported previously[13].



(2)

Namely, the hexa-substituted C-C bond in 3 is dissociated into propagating radical (4), and a less-reactive radical (2, X= CN), the former reacts with MMA to induce polymerization, whereas the latter undergoes PRT by recombination leading to 3 with the identical C-C bond. Chain transfer of 4 to the hexa-substituted C-C bond in 3 gives rise to produce 4 and 3, and it does not affect the pattern of reactions.

In the previous paper [30], the model compound for 3 (X= CN), methyl 2,2-dimethyl-3,3-diphenyl-3-cyanopropionate, was found to initiate living radical polymerization of MMA. Similar observations were also reported for 3 (X= C_6H_5) [22]. In addition, Braun and coworkers [11] observed that the oligomers isolated from polymerization of MMA with 1 (X= OC_6H_5, and CN) induced radical polymerization of MMA. These results indicate that the hexa-substituted C-C bond in 3 (X= OC_6H_5, CN and C_6H_5), which is also considered to be a dormant propagating radical species, is dissociated into 4 and 2.

However, the observed relations between $\bar{M}$ and conversion shown in Figure 3 do not pass the origin and the increase in $\bar{M}$ is relatively small. These observations may be accounted for by the fact that the living nature is not so high, because undesirable side reactions leading to deactivation of the active chain end (iniferter site) occur in competition with Eq. 2. The possible side reactions are ordinary bimolecular terminations between 4, PRT by disproportionation between 4 and 2, nuclear-substitution of 4 to the benzene ring in 2, and initiation with 2, as described in previous papers [22,30]. When TPSN and TMPSN were used, the last side reaction seems to be the most important.

As described before, an induction period appeared in the polymerization of MMA with TPSN, when its concentration increased and the polymerization temperature decreased. To clarify this point, the GPC analysis of the polymerization mixtures was made as a function of reaction time. The results are shown in Figure 4, from which the TPSN disappeared and simultaneously the oligomer, which was soluble in methanol, was produced during the induction period (see Figure 2). After that the polymer was formed, and concurrently the peak due to the oligomer decreased.

To isolate the oligomer, the polymerization mixture of MMA (5 mL) and TPSN (19.2 mg, 1 x 10^{-2} mol/L) heated at 70°C for 2 hr was poured into a large amount of n-hexane. The oligomer ($\bar{M}$ = 2500) of 54.7 mg was isolated. The ^{1}H- and ^{13}C-NMR spectra are shown in Figure 5.

In ^{1}H-NMR spectrum, the peaks due to α-methyl protons (0.9, 1.0, 1.2 ppm), methylene protons (1.9 ppm), methoxy

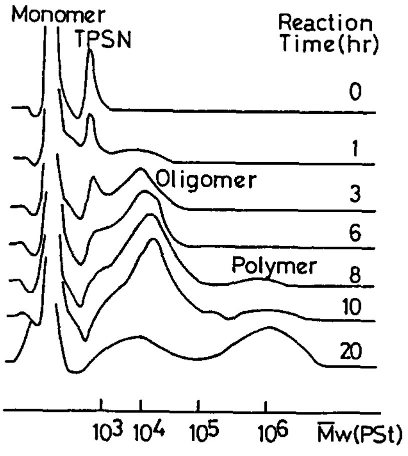


Figure 4 Change in GPC curves of the polymerization mixtures with reaction time for bulk polymerization of MMA with TPSN (1 x 10^{-2}mol/L) at 60°C

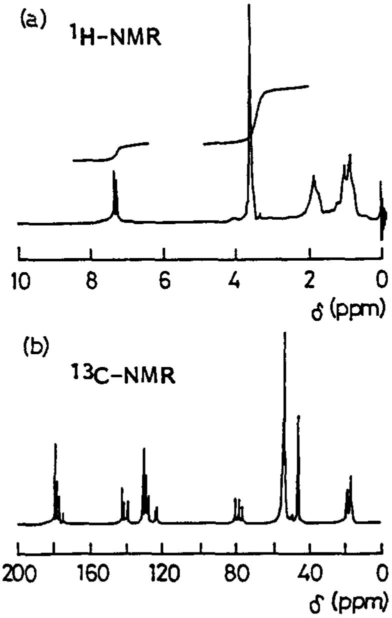
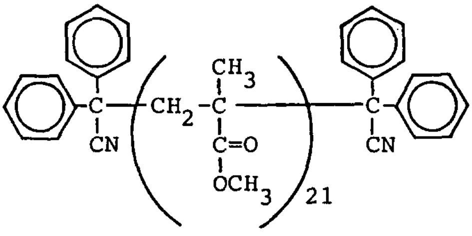


Figure 5 NMR spectra of the MMA-oligomer, 5.

protons (3.6 ppm) and aromatic protons (7.3-7.4 ppm) are observed. Similar results were also found in ^{13}C-NMR analysis. From the intensities of these peaks observed in the former spectrum, the oligomer isolated was reasonably assumed to be of the following structure, 5.

To know whether the oligomer 5 can induce radical polymerization, the bulk polymerization of MMA with 5 was attempted with various concentrations of 5 at 80 °C. The results are shown in Figure 6, from which this oligomer was found to induce polymerization without induction period, but with autoaccelerating effect similar to that with TPSN (see Fig. 2). From the log-log plots of the initial rates of polymerization with the concentration of 5, the reaction order was obtained as 0.25, indicating that these polymerizations were also performed by a living radical mechanism (Eq. 2).



Similarly the polymers produced by TPSN and PPE were also found to induce the polymerization of MMA, in which both yield and $\bar{M}$ increased as a function of reaction time. Moreover, the polymers thus obtained were shown to initiate again the polymerization of MMA.

The results of block copolymerization of St with poly(MMA)s prepared with TPSN, PPE and AIBN are shown in Table 2. The poly(MMA) produced by AIBN gave a minor part (12%) of block copolymer. However, when the poly(MMA)s obtained with TPSN and PPE were used, the block copolymers were obtained in 37-58% yields, i.e.

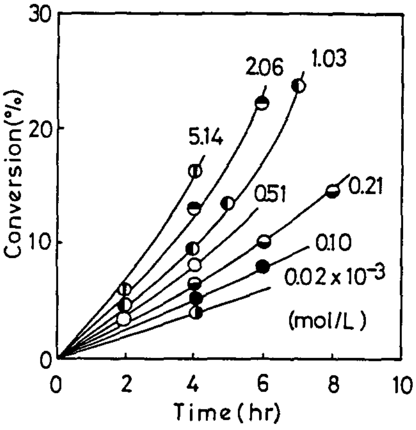


Figure 6 Time-conversion relations for bulk polymerization of MMA with 5.

Table 2 Results of Block Copolymerization of St with Poly(MMA) Prepared by TPSN, PPE and AIBN[a)]

Poly(MMA) used		Yield	Fraction extracted (%)		
Prepared by[b)]	(g)	(g)	Homo-poly(MMA)	Homo-poly(St)	Block copolymer
TPSN/70 °C/10hr	0.40	1.44	23.0	32.8	44.2
TPSN/90 °C/4hr	0.35	1.42	32.6	30.1	37.3
PPE/60 °C/8hr	0.40	1.56	14.3	27.1	58.4
PPE/60 °C/20hr	0.40	1.43	18.0	37.1	44.9
AIBN/60 °C/0.5hr	0.30	1.80[c)]	14.9	72.9	12.2

a) Copolymerization conditions: St 10 mL, at 80 °C for 12 hr.
b) [TPSN] = [PPE] = [AIBN] = 1 x 10^{-2} mol/L. c) For 20 hr.

a considerable amount (42-63%) of the homopolymers was produced. These results are accounted for by low living nature.

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