

# Synthesis of Block Copolymers by the Combination of Chain Transfer Polymerization and Initer Process

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## SYNOPSIS

Radical polymerizations of styrene (St) and methyl methacrylate (MMA) were carried out in the presence of tri phenylmethyl mercaptan (TPMM) as a chain transfer agent to give trityl (triphenylmethyl) terminated polymers. Transfer constants were found to be 17.8 and 0.71 for St and MMA, respectively. Trityl terminated polymers served as thermal "INITERS" for polymerization of vinyl monomers which proceeded via a quasi-living radical mechanism. This procedure makes it possible to prepare block copolymers. © John Wiley & Sons, Inc.

## INTRODUCTION

There have been several classical methods for the preparation of block copolymers, which generally involve the successive polymerization of two or more monomers by the same mechanism. Transformation reactions extend the range of possible monomer combinations in block copolymer.<sup>1,2</sup> This approach allows polymers produced by one type of polymerization to be terminally functionalized by groups capable of initiating a different mode of polymerization. We have previously reported the synthesis of block copolymers by cationic and radical,<sup>3,4</sup> anionic and radical,<sup>5</sup> condensation and radical,<sup>6-9</sup> redox and thermal radical,<sup>10,11</sup> and thermal radical and photochemical radical polymerization<sup>12-15</sup> routes.

The iniferter method, for the preparation of block copolymers, has been extensively explored during the last decade, primarily by Otsu et al.<sup>16</sup> In this concept, iniferters (*initiator-transfer agent-terminator*) were used to design the structure of polymer chain ends in radical polymerization.<sup>17</sup> Several organic disulfides and phenylazo triphenylmethane were found to serve as photo and thermal iniferters,<sup>16,18</sup> respectively. Polymers, obtained by using iniferters, still have iniferter function capable of

initiating the polymerization of another monomer yielding block copolymers.

It has been shown that radical transfer polymerization can be used successfully for the preparation of polymers with functional end groups. Chujo et al. recently prepared carboxy<sup>19</sup> and crown-ether terminated<sup>20</sup> poly(methyl methacrylate) (PMMA) using appropriate mercapto compound.

On the basis of these approaches, the present article deals with the possibility of the synthesis of polymers with terminal trityl (triphenylmethyl) group, using the corresponding chain transfer compound, capable of acting as a thermal "initer" (*initiator-terminator*), and its further use for the preparation of block copolymers.

## EXPERIMENTAL

Triphenylmethyl mercaptan (TPMM) was used as purchased. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. All solvents and monomers were purified by conventional drying and distillation procedures.

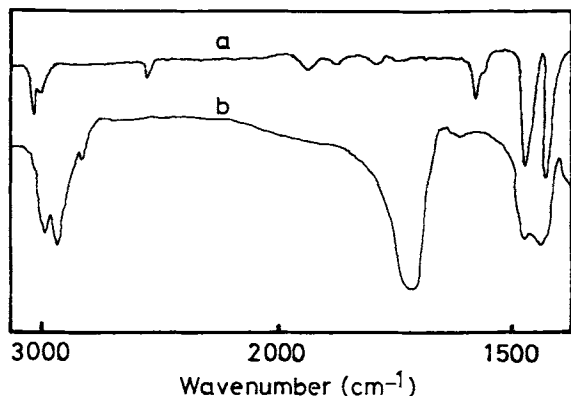
IR spectra were recorded on a Shimadzu IR-400 model spectrophotometer. <sup>1</sup>H-NMR spectra were obtained with a Bruker 200 spectrometer in CDCl<sub>3</sub> solution with tetramethyl silane as internal standard. The *P<sub>n</sub>* values were calculated from GPC chromatograms, according to standard polystyrene

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**Figure 1** IR spectra of (a) TPMM and (b) TPM-PMMA.

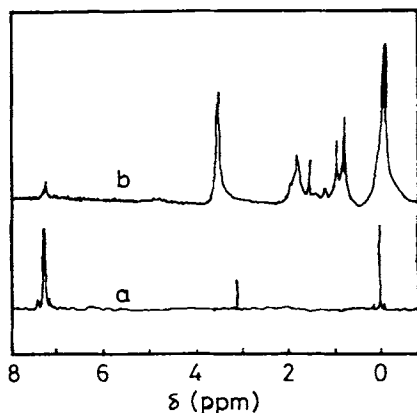
samples, using a Knauer M-64 instrument and ethylmethyl ketone as the eluent at flow rate of 1 mL/min.

#### Preparation of Trityl Terminated Polymers

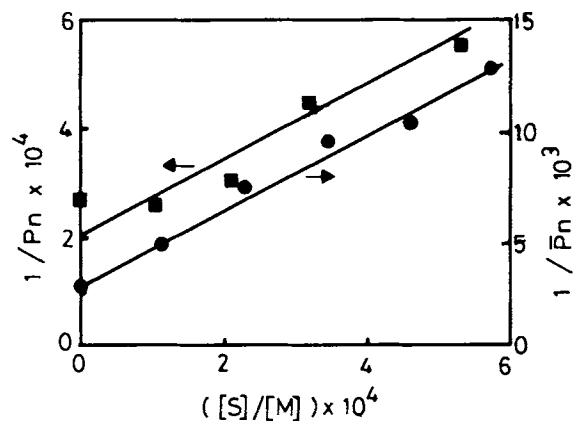
Bulk monomers, containing a known amount of AIBN and TPMM, were outgassed in the usual manner and were placed in a constant temperature bath at 70°C. At the end of reaction, the mixtures were poured into a ten-fold excess of methanol, and precipitated polymers were then filtered and dried.

#### Block Copolymerization

Bulk monomers, containing the trityl terminated polymers obtained above, were degassed and were heated at 70°C. After polymerization for a given



**Figure 2** <sup>1</sup>H-NMR spectra of (a) TPMM and (b) TPM-PMMA.

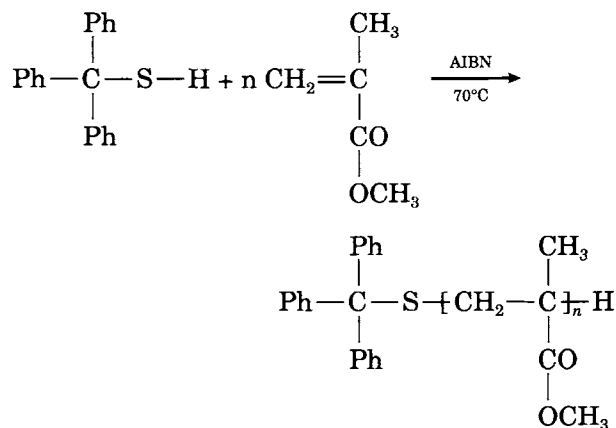


**Figure 3** Plots of reciprocal degree of polymerization vs.  $[S]/[M]$  for (●) St and (■) MMA polymerization, S = TPMM.

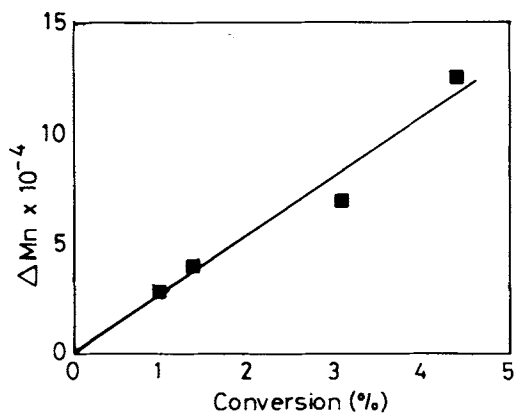
time, the contents of the tubes were poured into methanol. The separation of the polymers, obtained from block copolymerization, was carried out by extracting them with appropriate solvents.

#### RESULTS AND DISCUSSION

Styrene (St) and methylmethacrylate (MMA) were polymerized in the presence of AIBN and TPMM as initiator and chain transfer agent, respectively, yielding polymers with trityl end groups as depicted below. That is, for MMA polymerization:



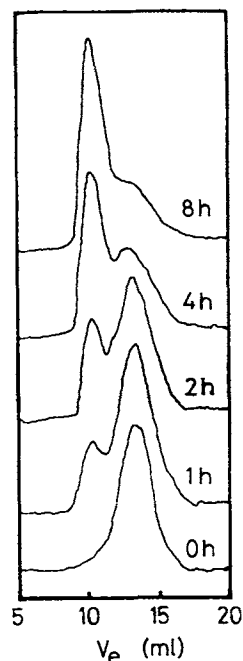
Typical IR spectra of TPMM and trityl terminated PMMA (TPM-PMMA) are illustrated in Figure 1. The stretching band at  $2570\text{ cm}^{-1}$ , due to S-H group, disappeared in the polymer. Figure 1(b) also shows the trityl moiety IR peaks, together with



**Figure 4** Polymerization of St with TPM-PSt at 70°C. [St] = 8.7 mol/L, [TPM-PSt] = 20 g/L ( $\bar{M}_n = 12000$ ),  $\Delta\bar{M}_n = \bar{M}_{n_i} - \bar{M}_{n_0}$ .

the peaks for PMMA. The introduction of trityl groups into PMMA was also supported by  $^1\text{H-NMR}$ . As can be seen from Figure 2, aromatic protons appear in the 7.2 ppm region, in addition to peaks at 3.6 and 1.4–2.0 ppm for  $\text{OCH}_3$  and vinyl protons, respectively. The UV spectrum of the polymer possesses an absorption band at around the 330 nm region, indicating attachment of trityl end groups. In addition, GPC analysis shows no contamination by physically entrained TPMM in the polymer.

TPMM was shown to be an efficient transfer agent in the polymerization of St and MMA. Transfer constants were found to be 17.8 and 0.71 for St and MMA, respectively, from the slope of  $1/\bar{P}_n$  against  $[\text{S}]/[\text{M}]$  as shown in Figure 3. Notably, the chain transfer constant for St is higher than that for MMA polymerization. In general, the same be-



**Figure 5** GPC traces for polystyrene polymerized in bulk with TPM-PSt at each time.

havior was observed with common chain transfer agents.

#### Radical Polymerization with Polymeric Thermal Initiator

The polymer obtained has a trityl moiety at one end. Trityl terminated polystyrene (TPM-PSt) was used as a thermal initiator in the polymerization of St. The plot of mol wt change of the polymers ( $\Delta\bar{M}_n = \bar{M}_{n_i}$

**Table I** Block Copolymerization by Using Polymeric Initiators

Polym. Initiator (g/L)	Monomer (mol/L)	Time (h)	Yield (g)	Fractions Extracted		
				PSt (%)	PMMA (%)	Block (%)
TPM-PSt, 80 (49800)	MMA, 9.4	3	0.72	22	26	52 (110700)
TPM-PMMA, 40 (110600)	St, 8.7	2	0.52	22	16	62 <sup>a</sup> (142500)
TPM-PMMA, 40 (106800)	St, 8.7	2	0.56	15	19	66 (145800)

Numbers in parenthesis show the  $\bar{M}_n$  values.

<sup>a</sup> Block copolymer composition: 19.4% St determined by NMR; 21.7% St determined by GPC.

–  $\bar{M}n_o$ ) against the conversion is shown in Figure 4. Here,  $\bar{M}n_i$  and  $\bar{M}n_o$  denote mol wt of the polymer recorded after various polymerization times and of the prepolymer, respectively. As can be seen,  $\Delta\bar{M}n$  of the polymers increased linearly with conversion, which indicates that this polymerization proceeds via a quasi-living radical mechanism in a manner proposed by Otsu et al.<sup>16</sup> Figure 5 shows the GPC traces recorded with polymer isolated at various reaction times in bulk polymerization of St with TPM-PSt. The GPC trace of TPM-PSt showed unimodal mol wt distribution, but that formed thereafter became a bimodal mol wt distribution, that is, a new peak, due to higher mol wt polymer, appeared and shifted to the higher mol wt side with time. In relation to this, the peak for lower wt polymer decreased and that of higher mol wt polymer increased.

Thermal instability of trityl terminated polymer was proved by heating this polymer in boiling benzene for 3 h at 80°C. The resulting polymer showed no initiation activity for styrene polymerization and mol wt of the polymer in the presence of styrene did not change upon heating at 70°C. These results indicated that the polymer obtained by using TPMM as chain transfer agent was stabilized by such treatment and initiation functionality was due to trityl end groups. According to Otsu et al.<sup>16</sup> stabilized polymers exhibited thermal properties the same as those obtained with AIBN, as was concluded from TGA studies.

Polymerization involves dissociation of trityl terminated polymer into radicals to give chain extended high mol wt polymer. Bond dissociation is expected to occur preferentially at the S–CPh<sub>3</sub> bond, since tertiary bonds ease the decomposition. The thiyl radical reacts with the monomer, whereas the trityl radical reacts only with the propagating radical.

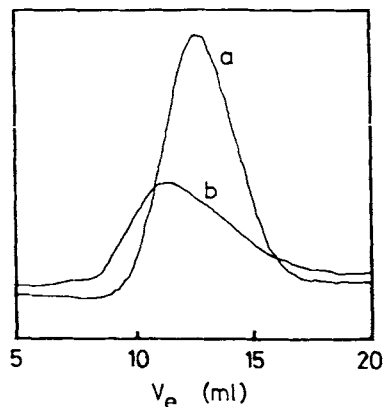
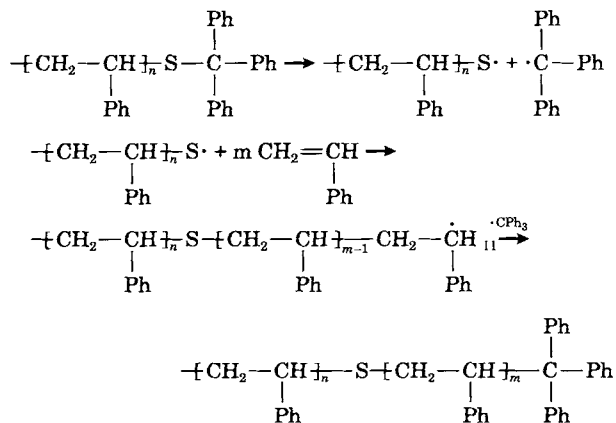


Figure 6 GPC traces for (a) TPM-PSt and (b) block copolymer of St and MMA.

Similarly, if the polymers thus obtained were used as polymeric initiators of the polymerization of second monomer, block copolymers must be produced. The results of block copolymerization of St with TPM-PMMA and MMA with TPM-PSt are summarized in Table I. Block copolymers were freed from homopolystyrene and homopoly(methylmethacrylate) by extracting them from boiling cyclohexane and acetonitrile, respectively. As can be seen, apart from the block copolymer, a considerable amount of homopolymer is formed, which may be due to thermal, uncatalyzed polymerization of the second monomer, since the thiyl radical is a weaker initiating species. Additionally, polymer molecules, which for many reasons fail to acquire trityl groups during the chain transfer polymerization, contribute to the formation of nonblocked components. Several deactivation reactions, leading to the formation of homopolymers, have been discussed in detail elsewhere.<sup>18</sup>

Representative GPC traces for TPM-PSt, and after polymerization with MMA, are shown in Figure 6. The peak at higher mol wt is ascribed to the block copolymer.

In conclusion, these results indicate that the combination of chain transfer polymerization and the initer technique can be applied to produce a block copolymer of monomers that are prone to free radical polymerization. This method pertains to trityl groups attached to the polymer ends by means of high chain transfer reactions and subsequent thermalolysis of these groups in the presence of monomers.

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