Synthesis of the styrene and methyl methacrylate block copolymer using a polymer of pentamethylene disulphide

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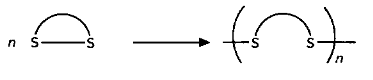
Photo block copolymerization of styrene with methyl methacrylate was studied using polymers obtained from the polymerization of styrene with a polymer of pentamethylene disulphide. The block copolymer was synthesized with a high block efficiency.

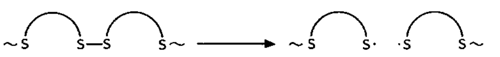
(Keywords: block copolymerization; styrene; methyl methacrylate; pentamethylene disulphide; polymeric initiator; radical polymerization)

Introduction

Many approaches have been proposed for synthesizing block copolymers using chain mechanisms[1–3]. Since a variety of monomers can be utilized in radical polymerization, block copolymers of many combinations of vinyl monomers have been synthesized using iniferters[4–7] and polymeric initiators bearing azo groups[8] or peroxide groups in the main chain[9].

Cyclic disulphides can be polymerized via a radical mechanism to give polymers containing disulphide bonds in the main chain [equation (1)][10–13], and these bonds cleave under u.v. irradiation to give a thiyl radical [equation (2)][14]. This indicates that polymers of cyclic disulphides can be used as polymeric radical initiators.


(1)


(2)

In block copolymer synthesis via a radical mechanism, homopolymers of each block segment are usually produced, leading to a decrease in block efficiency. However, we found that block copolymer synthesis using a polymer of cyclic disulphide showed a high block conversion.

This communication reports the synthesis of block copolymers of styrene (St) and methyl methacrylate (MMA) using polymers of pentamethylene disulphide (PMDS) which is a seven-membered cyclic disulphide.

Experimental

Materials. PMDS was synthesized by a known method[15]. St and MMA were purified by distillation before use. Other reagents were purified by conventional procedures. The polymer of PMDS (PPMDS) was prepared by radical polymerization with benzoyl peroxide (BPO) in benzene at 60°C. The PPMDS used for block copolymerization had a number-average molecular weight $\bar{M}_n$ of 39.2×10^4 and a polydispersity ($\bar{M}_w/\bar{M}_n$) of 3.4.

Polymerizations. Polymerizations were carried out in a sealed glass tube by irradiation using a Toshiba SHL-100 u.v. lamp from a distance of 10 cm. After polymerization the contents of the tube were poured into methanol to precipitate the polymers. The polymers were washed well with methanol and dried *in vacuo* at room temperature. The polymer yield was determined by gravimetry.

Characterization. Separation of the resulting polymers into homopolymer and block copolymer was carried out by extracting with suitable solvents, i.e. acetonitrile for PMMA and cyclohexane for polystyrene[4]. $\bar{M}_n$ and $\bar{M}_w$ were determined by g.p.c. at 38°C using THF as an eluent. Polystyrene standards were used for calibration. The polymer structure was checked by n.m.r. spectroscopy using a JEOL GX-400 spectrometer.

Results and discussion

To synthesize block copolymers of St and MMA, polymerization of St with PPMDS was carried out by u.v. irradiation at 30°C. The results are summarized in *Table 1*. The polymerization of St proceeded to give solid polymer having $\bar{M}_n$ of $15.5 \times 10^4 - 18.2 \times 10^4$. In the absence of St, a breakdown of PPMDS was observed to give an oligomer[14]. In the absence of PPMDS only a small amount of polystyrene was formed. These findings indicate that PPMDS is effective for the polymerization of St.

If these polymers still contain disulphide bonds in the chain, they may be used as parent polymers for block copolymerization with MMA. After the parent polymers were purified by precipitation, block copolymerization with MMA was carried out by u.v. irradiation at 30°C. The results are given in *Table 2*. Copolymerization with MMA took place, though the rates were low.

The resulting polymers were extracted with cyclohexane and then with acetonitrile to remove the homopolymers of St and MMA, respectively. It is clear from *Table 2*

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Table 1 Bulk polymerization of St with PPMDS by u.v. irradiation at 30°C[a]

Sample no.	[PPMDS] (g dm^{-3})	[St] (mol dm^{-3})	Time (h)	Yield (%)	$\bar{M}_n$[c] ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$[c]
1	3.9	8.7	20	8.4	18.2	3.4
2	3.9	8.7	40	14.7	15.5	5.3
3	5.5[b]	–	10	–	0.5[c]	4.7[c]
4	–	8.7	10	0.4	169.0	3.6

[a] PPMDS was obtained from the polymerization of PMDS with BPO at 60°C ($\bar{M}_n = 39.2 \times 10^4$, $\bar{M}_w/\bar{M}_n = 3.4$)
[b] In benzene
[c] PPMDS recovered after reaction

Table 2 Block copolymerization with MMA by polystyrene-PPMDS by u.v. irradiation at 30°C for 10 h

			Extraction (wt%)			Block copolymer	
[Polystyrene-PPMDS][a] (g dm^{-3})	[MMA] (g dm^{-3})	Yield[b] (%)	Homo polystyrene	Homo PMMA	Block copolymer	$10^{-5}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
4.0	9.4[c]	4.8	0.0	10.4	89.6	18.9	2.5
2.0	4.7[d]	3.8	0.0	11.0	89.0	19.6	2.0

[a] Sample no. 2 from *Table 1* was used
[b] Polymer yield of MMA
[c] Polymerized in bulk
[d] Polymerized in benzene

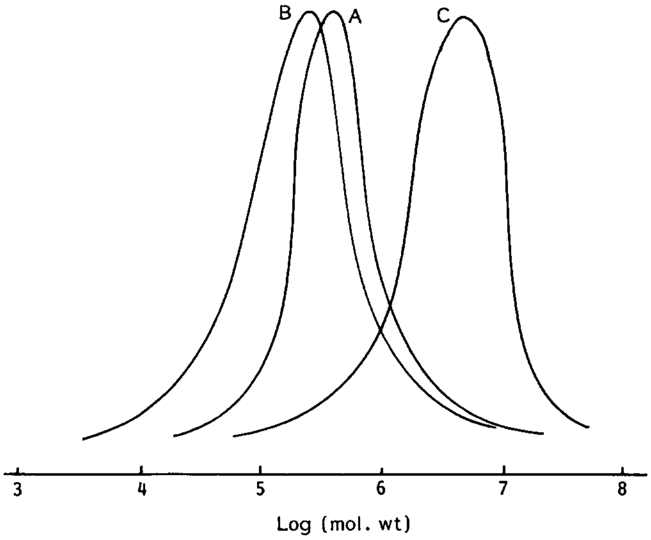

Figure 1 G.p.c. elution curves for (A) PPMDS, (B) polystyrene obtained with PPMDS and (C) polystyrene-*block*-poly(methyl methacrylate)

that no cyclohexane-soluble fraction was obtained, suggesting that the chain of St homopolymer obtained from the polymerization of St with PPMDS contains PMDS units. On the other hand, small amounts of an acetonitrile-soluble fraction were extracted, and confirmed to be the MMA homopolymer by i.r. and ^{13}C n.m.r. spectra; the remainder was the block copolymer.

G.p.c. elution curves of the polymers are shown in *Figure 1*. After block copolymerization with MMA, the curve of the block copolymer is clearly shifted towards higher molecular weight and no peaks corresponding to the parent polymer were observed. The presence of both St and MMA segments was confirmed by ^{13}C and ^{1}H n.m.r. spectra, but the sequence of PMDS units was not observed significantly. Accordingly, the resulting polymer is considered to be a block copolymer of St and MMA segments, but the type of block copolymer is not clear.

The block efficiency was determined as the ratio of the weight of the block copolymers obtained to that of the total polymer formed. The results are listed in *Table 2*. The efficiency was determind to be ~90%.

In conclusion, block copolymers of St and MMA were synthesized using PPMDS as a polymeric initiator. This method gave a high block efficiency, and may be applied to other cyclic disulphides.

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