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Efficient Synthesis of Two or Multi Component Block Copolymers Through Living Radical Polymerization with Polymeric Photoiniferters

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Summary

To synthesize efficiently block copolymers, the radical polymerization of vinyl monomers with the polymers obtained by tetraethyl thiuram disulfide(TD) as polymeric photoiniferters has been investigated. These photopolymerizations were found to proceed via a living radical mechanism, i.e. both the whole polymer yields and the average molecular weight of the block copolymers increased with increasing of the polymerization time. By applying these living radical polymerizations, various block copolymers consisting of two, three and four component blocks were obtained in good yields, suggesting that these techniques are effective and useful for synthesizing multi component block copolymers through radical polymerizations of polar vinyl monomers.

Introduction

In recent papers[OTSU et al., 1982a, 1982b], we reported that vinyl polymerizations in homogeneous solution with some organic sulfides as tetraethyl thiuram disulfide(TD) as photoiniferters[OTSU et al., 1982c] were performed by a living radical mechanism. In these cases, the C-S bond at the propagating polymer chain ends is dissociated photochemically into a reactive propagating radical and a small radical which undergoes only recombination with the counterpart polymer radical to reform the C-S bond, and hence monomer molecules are inserted successively into this dissociated bond.

This new model for a living radical polymerization was realized from the facts that the molecular weight of the polymers increased with the reaction time(i.e. conversion) and the numbers of the end groups per one polymer molecule were kept constant independent of the reaction time, i.e. conversion[OTSU et al., 1982b].

The other important support was also obtained from the formation of block copolymers through these systems, which was found in 25 years ago[OTSU, 1957, 1959] i.e. the photopolymerization of methyl methacrylate(MMA) with polystyrene obtained by TD gave a block copolymer. Subsequently, the block copolymers of polystyrene(PSt) with polyvinyl acetate(PVAc) or polyvinyl alcohol(PVA) were prepared efficiently by this method[OTSU et al., 1960].

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Therefore, a study was attemped to reexamine these results from a viewpoint of the present new concept, and various block copolymers consisting of two, three and four(multi) component blocks were found to be easily synthesized in good yields. The results obtained will be described in this paper.

Experimental Part

Monomers, solvents and precipitants were used after ordinary purifications. The PSt and PMMA bonded the N,N-diethyldithiocarbamate[$(C_2H_5)_2NCSS-$] group at the polymer chain ends(TD-PSt and TD-PMMA, respectively)(see 1) which were used as polymeric photoiniferters were prepared through their bulk polymerizations with TD at 60°C, and purified by reprecipitating them three times from the benzene-methanol system.

The block copolymerizations were carried out in sealed tube under irradiation of Toshiba SHL-100 UV lamp from a distance of 10 cm. After polymerization for a given time, the contents of the tube were poured into a large amount of suitable precipitants to isolate whole polymers. The precipitants were used as methanol for PSt, PMMA and polyacrylonitrile(PAN), n-hexane for PVAc and polyethyl acrylate(PEA), and petroleum ether for PVAc.

The separation of the resulting whole polymers into two homopolymers and a block copolymer was carried out by extracting them with suitable solvents, i.e. cyclohexane, acetonitrile and methanol for PSt, PMMA and PEA or PVAc, respectively. The polymer fractions extracted were checked by their IR spectra.

The intrinsic viscosities($[\eta]$) were determined viscometrically in benzene at 30°C, and then the average molecular weight were calculated by the following equations:

For PSt[ALTARES et al., 1964]: $[\eta]=8.5\cdot10^{-5}\bar{M}^{0.75}$ (1)

For PMMA[FOX et al., 1962]: $[\eta]=6.27\cdot10^{-5}\bar{M}^{0.76}$ (2)

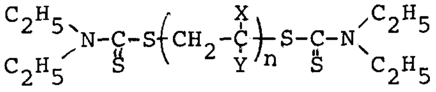
For PVAc[NAKAJIMA, 1954]: $[\eta]=56.3\cdot10^{-5}\bar{M}^{0.62}$ (3)

For PEA[SUMITOMO et al., 1955]: $[\eta]=27.7\cdot10^{-5}\bar{M}^{0.67}$ (4)

For some polymer samples, the number-average molecular weights($\bar{M}_n$) were determined in toluene at 31°C by a membrane osmometry. The molecular weight distribution was measured by a gel permeation chromatography(GPC).

Results and Discussion

TD-PSt and TD-PMMA used as polymeric photoiniferters in this study were confirmed by both end-group and $\bar{M}_n$ determinations to consist of the following structure(1)[OTSU et al., 1982b]:



$$(C_2H_5)_2N-\underset{\|\atop S}{C}-S\left(CH_2-\underset{Y}{\overset{X}{C}}\right)_n S-\underset{\|\atop S}{C}-N(C_2H_5)_2$$

1 { $X=H$, $Y=C_6H_5$: TD-PSt
$X=CH_3$, $Y=COOCH_3$: TD-PMMA

The plots of the yield of whole polymers and the $\bar{M}$ of the block copolymers separated(see Table 1) against the polymerization time in the photopolymerizations of MMA with TD-PSt are shown in Fig. 1. From this figure, both the yield and the $\bar{M}$

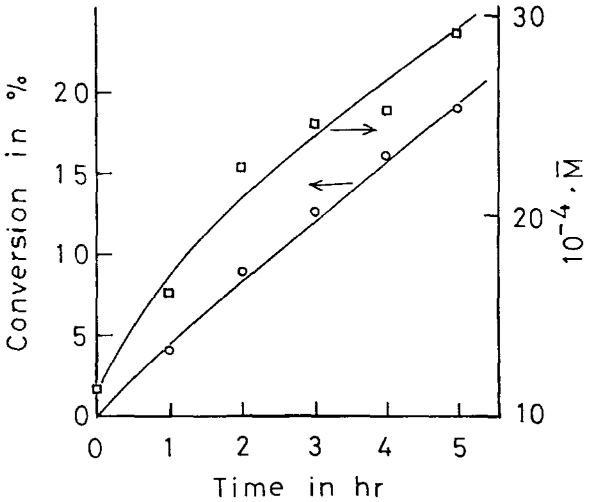


Fig. 1 Photopolymerization of MMA with TD-PSt at 30°C: [MMA]=4.0 mole/l, [TD-PSt]=4.0·10^{-2}g/ml

are found to increase as a function of polymerization time, strongly indicating that this polymerization proceeds via a living radical mechanism as well as that by TD or benzyl N,N-diethyldithiocarbamate as photoiniferters[OTSU et al., 1982a, 1982b].

Similar result was also obtained for photoblock copolymerization of VAc with TD-PSt. The results of GPC curves of two homopolymers(TD-PSt and PVAc) and a block copolymer separated from photopolymerization of VAc with TD-PSt are shown in Fig. 2, from which the molecular weight distribution of the block copolymer obtained is seen to shift to a high molecular weight side than that of PSt and PVAc. From this result and the observed increase in molecular weight(see Table 1), it is clear that the block copolymer was obtained through such a polymerization. Moreover, from thermogram shown in Fig. 3, this block copolymer degrades with two different maximum temperatures at 350°C and 410°C, which seem to correspond to PVAc and PSt blocks, respectively.

Table 1 summarizes the results of block copolymerizations by using TD-PSt or TD-PMMA as polymeric photoiniferters. From this table, it is found that the block copolymers, which have higher $\bar{M}$(or $\bar{M}_n$) than those of the respective homopolymers, are found in good yields above 70% from these systems.

From comparing the $\bar{M}_n$ and $\bar{M}$ of the block copolymers observed and calculated(see footnote in Tab. 1, respectively) with those calculated theoretically, the type of block copolymers may be deduced. These results are also indicated in Table 1, from which the block copolymers obtained are found to consist of the ABA type for (PSt-PVAc) or (PMMA-PSt), and the AB type for (PSt-PMMA) or (PSt-PEA). Such a difference seems to be originated from the reactivities of intermediate radicals produced from the dissociation of the $(C_2H_5)_2NCSS$- end groups toward second monomers used, as discussed in a previous paper [OTSU et al., 1982b].

Table 1 Results of Block Copolymerizations with TD-PSt or TD-PMMA at 30°C[a)]

Polymeric photoiniferter(g)	Second monomer (M_2)(ml)	Benzene (ml)	Time (hr)	Total yield (g)	Fractions extracted									Type of Block copolymer[d)]
					TD-polymer			M_2 homopolymer			Block copolymer			
					(%)	[η]	$\bar{M}\cdot 10^{-4}$	(%)	[η]	$\bar{M}\cdot 10^{-4}$	(%)	[η]	$\bar{M}\cdot 10^{-4}$ [b)]	
TD-PSt(0.84)	VAc(15)	9	40	1.99	3.1	0.33	6.1 5.3[c)]	23.0	0.35	3.2 4.8[c)]	73.9	0.67	12.4 12.0[c)]	ABA(12.5) ABA(14.9)
TD-PSt(0.84)	VAc(15)	9	40	2.05	3.4	0.21	3.3	24.5	0.28	2.2	72.1	0.59	10.1	ABA(7.7)
TD-PSt(0.30)	MMA(2)	5	6	0.70	0.0	0.52	11.2	21.5	0.36	8.8	78.5	0.71	19.2	AB (20.0)
TD-PSt(0.30)	MMA(2)	5	6	0.78	0.0	0.33	6.1 5.3[c)]	34.5	0.30	6.9 5.2[c)]	65.5	0.50	12.3 10.5[c)]	AB (13.0) AB (10.5)
TD-PSt(0.30)	EA(2)	3	1	1.95	6.2	0.52	11.2	12.6	1.21	27.1	81.2	1.59	43.4	AB (38.3)
TD-PSt(0.30)	EA(2)	3	1	2.12	3.2	0.33	6.1	17.8	0.83	15.5	79.0	1.04	23.7	AB (21.6)
TD-PMMA(0.30)	St(5)	5	12	0.63	3.5	0.34	8.2 6.4[c)]	19.8	0.38	7.4 4.4[c)]	76.7	0.97	29.4 24.1[c)]	ABA(23.0) ABA(15.2)
TD-PMMA(0.30)	St(5)	5	12	0.73	3.3	0.22	4.6	21.6	0.34	6.3	74.4	0.89	25.9	ABA(14.6)

a) Polymerized under irradiation of UV light from a distance of 10 cm.

b) Calculated by the following equation: $[\eta]^{2/3}_{block} = X[K\cdot\bar{M}^{\alpha}]^{2/3}_{PM_1} + (1-X)[K\cdot\bar{M}^{\alpha}]^{2/3}_{PM_2}$

where X is weight fraction of M_1 unit, and $K\cdot\bar{M}^{\alpha}$ are molecular weight-viscosity relationships [eqs.(1)-(4)] for respective homopolymers.

c) Determined in toluene at 31°C by membrane osmometry.

d) Values in parentheses were molecular weight calculated for AB or ABA type block copolymer

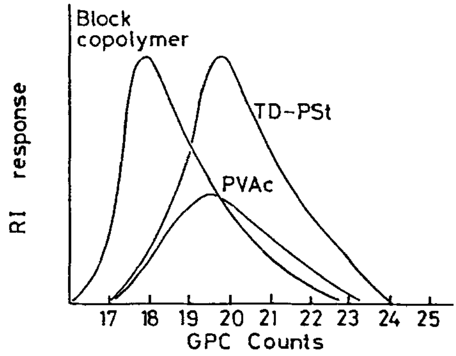


Fig. 2 GPC curves of TD-PSt, PVAc and PSt-PVAc block copolymer obtained from photopolymerization of VAc with TD-PSt at 30°C

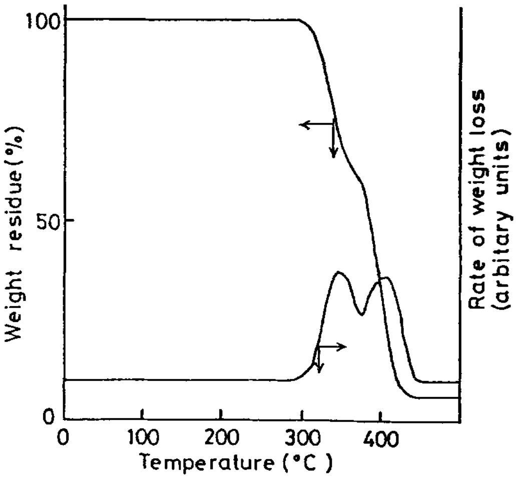


Fig. 3 Thermogram of the PSt-PVAc block copolymer

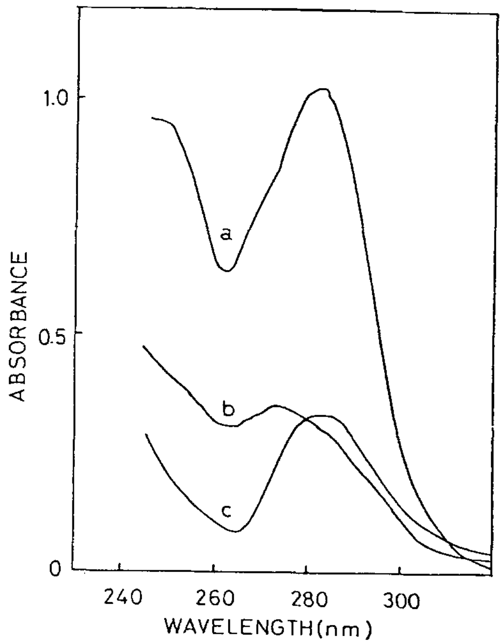


Fig. 4 UV spectra of block copolymers in chloroform: (a)TD-(PSt-PEA), (b)TD-(PMMA-PSt) and (c)TD-(PSt-PMMA)

Figure 4 shows the UV spectra of the block copolymers thus obtained. The absorption band at 278 nm due to the $(C_2H_5)_2NCSS$- end group still remains[about 60% for (PSt-PEA) and 25% for (PSt-PMMA) or (PMMA-PSt) block copolymers]. These results were in good agreement with those observed in living radical polymerizations with TD and benzyl N,N-diethyldithiocarbamate photoiniferters[OTSU et al., 1982a, 1982b], and with TD-PSt as polymeric photoiniferter(Fig. 1). However, a part of the $(C_2H_5)_2NCSS$- end group seems to be destroyed when the photoirradiation time increased.

Table 2 shows the results of block copolymerizations of AN with block copolymers obtained above, as polymeric photoiniferters, in order to prepare a three component block copolymers. These polymerizations were induced quite easily. The amounts of the benzene-soluble fractions, which were confirmed to be the respective unreacted block copolymers, were found to increase with decreasing of those of the residual end groups, indicating the formation of the three component block copolymers in benzene-insoluble fractions.

Table 2 Further Block Copolymerizations of AN with TD-block Copolymers[a)]

TD-block copolymer			Total yield	Bz-soluble fraction	Bz-insoluble fraction	
Type	(g)	$[\eta]^{b)}$	(g)	(g)	(g)	$[\eta]^{c)}$
TD-(PSt-PMMA)	0.173	0.38	0.681	0.097	0.584	4.9
TD-(PSt-PEA)	0.291	0.55	1.595	0.014	1.577	4.6
TD-(PMMA-PSt)	0.217	0.76	0.636	0.109	0.509	5.2

a) Polymerizations were carried out by using AN(3 ml) and benzene(Bz; 3 ml) at 30°C for 9 hours under irradiation of Toshiba SHL-100 UV lamp from a distance of 10 cm.
b) Determined in benzene at 30°C.
c) Determined in dimethylformamide at 30°C

The separation of PAN from these fractions was unsuccessful. However, the previous observation that AN did not give polymer without photoiniferter, but it was readily polymerized with methyl N,N-diethyldithiocarbamate as a model compound for this polymer end group under simillar conditions[OTSU et al., 1958], seems to strongly suggest the formation of the three component block copolymers. Actually these copolymers showed much higher intrinsic viscosities than those of original block copolymers.

In order to synthesize the four component block copolymers, the photopolymerizations of MMA and EA in the presence of three component block copolymers obtained above were attempted. These polymerizations were performed easily. For an example, when a mixture of TD-(PSt-PEA-PAN)(0.10 g), MMA(3 ml) and DMF (10 ml) was allowed to react at 30°C for 9 hours under irradiation of UV light, the polymer of 0.46 g, which consists of benzene-soluble and -insoluble fractions of 67.4 and 32.6%, respectively, was produced. Further separation was unsuccessful, but it might be considered that the benzene-insoluble fraction consisted of three and four component block copolymers.

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