polymer communications

Synthesis of completely-alternating block polymers

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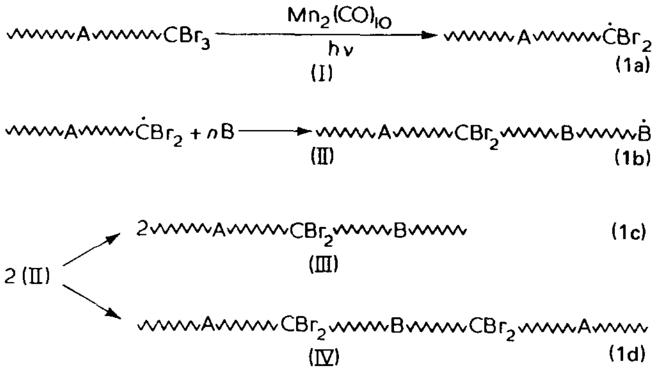
In this communication we report the synthesis of a novel type of block polymer in which all blocks are alternating copolymers

General synthetic routes to block and graft copolymers which utilize initiating systems based on organo-transition metal derivatives have been described in earlier papers[1,2]. Such systems incorporate a co-initiator, which may be an organic halide or an appropriate olefin or acetylene. We have used the former type in this work, but believe the latter would also be suitable.

To synthesize a simple block polymer, a preformed polymer of monomer A with reactive terminal halogen-containing groups is used as co-initiator in the polymerization of monomer B. The reactions are exemplified in (1a, b, c and d).



The nature of the product is determined by the character of the termination reaction in the polymerization of B; pure disproportionation (1c) and combination (1d) lead to two—or three—block polymers ((III) and (IV), respectively, while mixed termination gives rise to both species. At low conversions these will be the only products since the $-CBr_2-$ groups in (III) and (IV), being much less reactive than $-CBr_3$ in (I), do not participate significantly in initiation processes.

The first stage of the synthesis—the preparation of the preformed polymer—may be carried out by polymerizing monomer A in the presence of carbon tetrabromide as transfer agent; if the polymerization is initiated by an organo-transition metal derivative, CBr_4 also functions as co-initiator, generating CBr_3 radicals, so that all the polymer molecules formed have $-CBr_3$ and $-Br$ terminations. We have shown that the alternating copolymerization of some donor-acceptor monomer pairs (e.g. butadiene (Bd), isoprene (Ip) or styrene (St) with methyl acrylate (MA)) in the presence of the Lewis acid ethylaluminium sesquichloride ($Al_2Et_3Cl_3$) may be initiated in this way and, further, that carbon tetrabromide is an active transfer agent in these systems (although markedly less active than in the absence of Lewis acid)[3-5]. The alternating copolymers so prepared have the general structure (V)

$$Br \sim\sim ABAB \sim\sim CBr_3$$
(V)

(A = MA and B = Bd, Ip or St) except for a small fraction arising from the termination reaction (see below).

Note that the terminal bromine atom in (V) is very much less active than $-CBr_3$ in initiation.

In the second polymerization, the donor/acceptor monomer pair Y, Z is polymerized in the presence of a Lewis acid with (V) as co-initiator. The possible two- and three-block polymers resulting from reactions of the type shown in (1) are then:

$$Br \sim\sim ABAB \sim\sim CBr_2 \sim\sim YZYZ \sim\sim$$
(VI)

$$Br \sim\sim ABAB \sim\sim CBr_2 \sim\sim YZYZ \sim\sim CBr_2 \sim\sim ABAB \sim\sim Br$$
(VII)

We have synthesized, purified and characterized the following alternating block polymers (MMA = methyl methacrylate)

Poly(St-alt-MA)-block-poly(Ip-alt-MMA)-block-poly(St-alt-MA)
(VIII)

Poly(St-alt-MA)-block-poly(Bd-alt-MMA)-block-poly(St-alt-MA)
(IX)

Poly(Ip-alt-MA)-block-poly(St-alt-MMA)-block-poly(Ip-alt-MA)
(X)

Poly(Bd-alt-MA)-block-poly(St-alt-MMA)-block-poly(Bd-alt-MA)
(XI)

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Table 1 Synthesis of preformed alternating copolymers (V), λ = 436 nm

	Br-poly(St-alt-MA)-CBr$_3$	Br-poly(Ip-alt-MA)-CBr$_3$	Br-poly(Bd-alt-MA)-CBr$_3$
[St] (mol dm^{-3})	0.4	–	–
[Ip] (mol dm^{-3})	–	0.8	–
[Bd] (mol dm^{-3})	–	–	0.8
[MA] (mol dm^{-3})	0.4	1.6	1.6
[Al$_2$Et$_3$Cl$_3$] (mol dm^{-3})	0.075	0.2	0.2
[Mn$_2$(CO)$_{10}$] (mol dm^{-3})	2×10^{-3}	5×10^{-4}	5×10^{-4}
[CBr$_4$] (mol dm^{-3})	16×10^{-3}	8×10^{-3}	8×10^{-3}
Temperature (°C)	25	25	25
Reaction time (min)	45	45	45
Yield (base mol (A + B) dm^{-3})	0.56	0.34	0.19
$10^{-3}\bar{M}_n$	18	17	20
Bromine content (%)	2.36* (1.8)**	2.09 (1.9)	2.00 (1.6)

* From elemental analysis

** From molecular weight and structure (V)

Table 2 Synthesis and molecular weights of alternating block polymers. 25°C, [Mn$_2$(CO)$_{10}$] = 2×10^{-4} mol dm^{-3}, λ = 436 nm

Final block polymer		(VIII)		(IX)		(X)		(XI)	
Preformed copolymer		Br-poly(St-alt-MA)-CBr$_3$		Br-poly(St-alt-MA)-CBr$_3$		Br-poly(Ip-alt-MA)-CBr$_3$		Br-poly(Bd-alt-MA)-CBr$_3$	
10^4 concentration (mol dm^{-3})		8		8		8		6	
Concentrations of donor monomers (mol dm^{-3})	Ip	0.8							
	Bd			0.8					
	St					0.8		0.8	
[MMA] (mol dm^{-3}		1.6		0.8		0.8		0.8	
[Al$_2$Et$_3$Cl$_3$] (mol dm^{-3})		0.2		0.2		0.15		0.15	
Reaction time (min)		10	45	10	45	10	45	10	45
Ratio of donor monomers in fractionated block polymer	St/Ip	1/4.0	1/6.7			3.2/1	4.3/1		
	St/Bd			1/6.5	1/7.0			2.7/1	2.9/1
$10^{-3}\bar{M}_n$ calculated		163	249	194	240	178	228	197	209
$10^{-3}\bar{M}_n$ observed		123	220	268	286	161	217	–	296

Polymerizations were carried out in toluene solution at 25°C in the complete absence of oxygen in a laboratory illuminated by inactive (sodium) light, with photoinitiation ($\lambda = 436$ nm) by Mn$_2$(CO)$_{10}$. Polymers were isolated by precipitation into methanol. Details of the synthesis of the alternating copolymers used as co-initiators are presented in *Table 1*. Bromine contents of these copolymers were generally a little higher than calculated from their number-average molecular weights and structure (V), probably on account of the presence of molecules of structure (XII) arising from termination by combination.

$$Br_3C\sim\sim\sim ABAB\sim\sim\sim CBr_3$$

(XII)

The preformed copolymers (V) were found to be very active co-initiators in the second copolymerization as illustrated by *Figure 1*. Initial rates of polymerization ω are low in the absence of co-initiator, but, with increasing (V), first increase rapidly, pass through a flat maximum then decline somewhat. Apart from this latter feature, the curves have the form encountered with simple halide co-initiators. One factor contributing to the decline may be complexation between the co-initiator and Al$_2$Et$_3$Cl$_3$, which reduces the concentration of MA–Al$_2$Et$_3$Cl$_3$ complex. The maximum values of the rate of copolymerization are the same as those obtained by using CCl$_4$ (0.1 mol dm^{-3}) as co-initiator in the alternating copolymerization of the same monomer pair under the same conditions.

Table 2 shows details of the synthesis of the alternating block polymers. Purification of the latter from unreacted preformed polymer was carried out by fractional precipitation. For polymers (VIII) and (IX) methyl ethyl ketone (MEK) and methanol, and for (X) and (XI) toluene and cyclohexane, were used as solvent and precipitant, respectively. The precipitation ranges for 1% w/w solutions of alternating block polymers and the

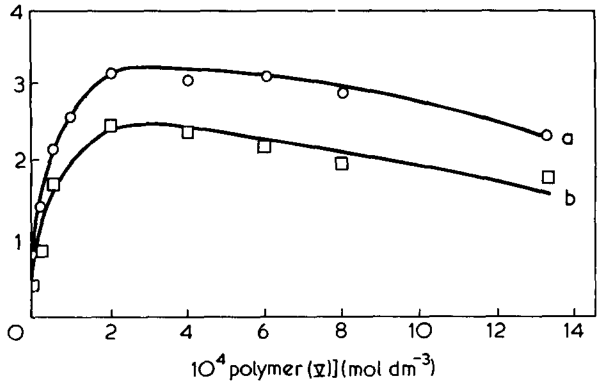

Figure 1 Dependence of rate of photo-initiated (λ = 436 nm) copolymerization ω on concentration of preformed alternating copolymer (V) (co-initiator). [Mn$_2$(CO)$_{10}$] = 2×10^{-4} mol dm^{-3}, 25°C, reaction time 10 min. (a), Copolymerization of St and MMA each 0.8 mol dm^{-3} in toluene. Co-initiator Br-poly(Bd-alt-MA)-CBr$_3$. [Al$_2$Et$_3$Cl$_3$] = 0.15 mol dm^{-3}; (b), copolymerization of Bd and MMA each 0.8 mol dm^{-3} in toluene. Co-initiator Br-poly(St-alt-MA)-CBr$_3$. [Al$_2$Et$_3$Cl$_3$] = 0.2 mol dm^{-3}

Table 3 Precipitation ranges for 1% w/w solutions of alternating block polymers and the preformed alternating copolymers

Polymer	Solvent	Precipitant	Precipitation range Volume ratio : precipitant/solvent
Poly(St-alt-MA)	MEK	methanol	1.3–2.2
Polymer (VIII)	MEK	methanol	0.7–1.1 (0.9)*
Polymer (IX)	MEK	methanol	0.9–1.2 (1.1)
Poly(Ip-alt-MA)	toluene	cyclohexane	no precipitation
Polymer (X)	toluene	cyclohexane	1.2–2.0 (1.8)
Poly(Bd-alt-MA)	toluene	cyclohexane	no precipitation
Polymer (XI)	toluene	cyclohexane	1.1–2.0 (1.8)

* Used for separating block polymer

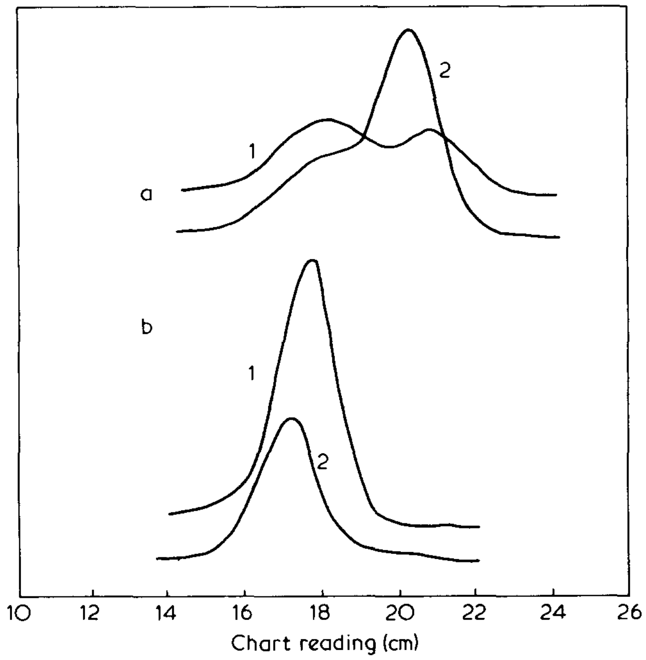

Figure 2 Purification of block polymer (VIII) by fractionation. G.p.c. traces: (a), unfractionated; (b), fractionated sample. Detection: 1 refractometer, 2 u.v. spectrophotometer (λ = 260 nm)

preformed alternating copolymers are set out in *Table 3*. The efficiency of the fractionation procedure is illustrated by the g.p.c. data in *Figure 2*. Similar results were obtained with all the polymers (VIII)–(XI).

The n.m.r. spectra of the block polymers (in $CDCl_3$ solution) were completely consistent with fully-alternating structures and permitted estimates to be made of the ratios of different types of unit in the polymers, notably St/Ip and St/Bd (*Table 2*). Since molecular weights of the preformed copolymers are known (*Table 1*), the molecular weights of the final polymers can be calculated with the aid of these ratios. Results are given in *Table 2*, from which it will be seen that reasonable agreement between calculated and observed osmometric values are obtained if the polymers have three-block structures (VIII)–(XI). Thus termination by radical combination (1d) must occur. The presence of two-block polymers would imply termination by disproportionation (1c) and/or chain transfer to preformed polymer in the second polymerization[6]. We conclude that either the fractionation removed any two-block polymers, or the two processes mentioned do not occur significantly.

We hope to report on the properties of these novel polymers subsequently.

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Potential artefacts in the determination of the optical anisotropy of macromolecules by light scattering

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A pronounced optical anisotropy of polymers in solution is a relatively rare phenomenon. The classical paper by Utiyama and Kurata[1] presents a detailed theoretical analysis of this phenomenon. A considerable optical anisotropy reflected in the high depolarization of scattered light was found experimentally by Utiyama with several (and with one in particular) fractions of isotactic polystyrene in chlorobenzene[2]. Reiss[3] observed the effect of optical anisotropy in light scattering measurements of solutions of atactic polystyrene in bromoform; the anisotropic character of the samples became less pronounced with increasing temperature. A similar trend in the change of optical anisotropy has been found by Utiyama and Tsunashima[4] for poly(α-methylstyrene) in *trans*-decalin. Carpenter *et al.*[5] have described marked anisotropic behaviour of filtered polyoxyethylene solutions in dioxan, in contrast with unfiltered solutions, where the optical anisotropy was negligible.

When studying light scattering from solutions of poly(methyl methacrylate) of various tacticities in butyl acetate, we also observed in several cases a pronounced depolarization of light incident on the photomultiplier, reflected among other things in typical concave angular dependences[1,2,5] of Kc/R_θ on $\sin^2(\theta/2)$ (*Figure 1*). However, in most solutions this effect has not been observed. The insertion of an antifluorescence filter did

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