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Blocking Group/Initiators for the Synthesis of Polyrotaxanes *via* Free Radical Polymerizations

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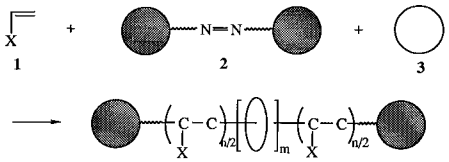
ABSTRACT: Two new blocking group/initiators (BG/inits) were prepared. 4,4′-Azobis[4-cyanopentanoic acid] (**7**) was converted to 4,4′-azobis[4-cyanopentanoyl chloride] (**8**). The acid chloride **8** reacted with 4,4-bis(*p-tert*-butylphenyl)-4-phenylbutanol (**5**) to give 4,4-bis(*p-tert*-butylphenyl)-4-phenylbutyl 4,4′-azobis-[4-cyanopentanoate] (**9**, BG/init **I**) in quantitative yield. 4-[Tris(*p-tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (**10**, BG/init **II**) was synthesized by room temperature esterification of 4,4′-azobis[4-cyanopentanoic acid] (**7**) with tris(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane (**6**) using the DCC coupling method. The results of the polymerization of styrene initiated by **I** and **II** indicated that both the BG/inits were well-behaved free radical initiators. Also, terminal group analysis by ^{1}H NMR spectra showed that the blocking efficiencies for polystyrene were 100% due to the termination *via* radical coupling. These BG/inits can be used as free radical initiators and blocking groups at the same time in the synthesis of polyrotaxanes prepared by radical polymerizations.

Introduction

Polyrotaxanes consist of cyclic molecules threaded onto linear polymer molecules.[1] Such physically combined molecular composites have been known since 1967,[2] and recently they have been gaining more interest in view of material science.[1, 3−5] Polyrotaxanes are distinct from conventional polymer blends because the two components can not be separated from each other unless chemical bonds of either or both components are broken. Also, polyrotaxanes are different from traditional copolymers due to the ability for the cyclic components to move along the linear chain and circumferencially. Thus, the potential area of utilization extends from simple property changes such as modification and enhancement of solubility, thermal stability, and interfacial bonding to preparation of specialty materials such as molecular level sensors and field-response materials.

Many traditional polyrotaxanes contain synthetic backbones such as polyamides,[1] polyurethanes,[3] and polyesters,[4] which are made from step growth polymerizations. In those cases the syntheses of the polyrotaxanes are achieved by condensation polymerizations of the corresponding monomers in the presence of macrocycles. Bulky species or blocking groups which contain suitable functional groups are introduced at the linear chain ends during the polymerizations to prevent threaded macrocycles from dethreading. Recently, we reported the synthesis of various triarylmethyl derivatives suitable for end blocking for this purpose.[6]

However, if the linear species are the polymers from olefinic monomers, it would not be easy to put the blocking groups at the chain ends. For instance, when we have synthesized poly(styrene−rotaxa-crown ether)s by anionic polymerization of styrene in the presence of crown ethers, in order to obtain thermodynamically stable polyrotaxanes, the living polymer chains were reacted with a blocking group which contained an alkyl chloride moiety.[7] This process required lots of experimental effort such as purifications of the reagents, inert atmosphere, and use of an excess amount of the blocking group to achieve complete blocking. Therefore, we designed and synthesized two new azo-type radical initiators **2** which can afford end-blocked polyrotaxanes **4** *via* free radical polymerizations of vinyl monomers **1** in the presence of cyclic species **3**.



In this paper, we report the synthesis of the blocking group/initiators (BG/inits) and the results of the poly-

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merization of styrene using the BG/inits as a demonstration of the utility of the BG/inits as free radical initiators and blocking groups for the synthesis of polyrotaxanes.

Experimental Section

Measurements. Melting points were taken in capillary tubes with a Haake-Buchler or Melt-Temp II melting-point apparatus. NMR spectra were obtained on a Bruker WP 270 MHz spectrometer or a Varian Unity 400 MHz spectrometer at ambient temperature using tetramethylsilane as an internal standard. GPC analyses of the polymers were performed at 20 °C in THF or $CHCl_3$ using a Waters system with a refractive index detector after calibration with PS standards or a Viscotek 100 differential viscometer detector using universal calibration. Elemental analyses were done by Atlantic Microlab of Norcross, GA. Computer molecular energy calculations were done using Cerius[2].[8]

***meso*-4,4′-Azobis[4-cyanopentanoyl chloride] (*meso*-8).** Repeated recrystallizations from ethyl alcohol and ethyl acetate separated 4,4′-azobis[4-cyanopentanoic acid] (**7**) (Aldrich Chemical Co.) as received into two isomeric forms, one melting at 141−143 °C and the other at 125−127 °C. The lower melting isomer was assigned as the *meso* isomer (*meso*-**7**).

A 50-mL 3-neck flask containing *meso*-4,4′-azobis[4-cyanopentanoic acid] (*meso*-**7**) (2.00 g, 7.14 mmol), thionyl chloride (40 mL; Aldrich Chemical Co.), a magnetic stirring bar, a thermometer, and a condenser with a drying tube was immersed into an oil bath preheated to 100 °C. At the end of 10 min the mixture was placed in an ice bath. The solution was cooled to room temperature, and the excess thionyl chloride was stripped off in vacuo. The resulting solid was dissolved in warm benzene and then precipitated with pentane. The solid was filtered under a nitrogen blanket and dried in a vacuum desiccator over calcium chloride. The yield was 2.0 g (88%) of a white powder with a melting point of 88−90 °C dec (lit. mp 93−95 °C,[9] 88−89 °C,[10] 89−90 °C[11]). ^{1}H NMR ($CDCl_3$, ppm): 1.55 (s, 6H), 2.45 (m, 4H), 3.05 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): 23.57, 32.91, 41.77, 71.24, 116.90, 172.15 (theory 6, found 6).

***meso*-4,4-Bis(*p-tert*-butylphenyl)-4-phenylbutyl 4,4′-Azobis[4-cyanopentanoate] (9).** In an oven-dried 25-mL 3-neck flask equipped with an addition funnel and a magnetic stirring bar were placed 4,4-bis(*p-tert*-butylphenyl)-4-phenylbutanol (**5**) (1.34 g, 3.24 mmol), THF (15 mL), and pyridine (0.30 g, 3.8 mmol). *meso*-4,4′-Azobis[4-cyanopentanoyl chloride] (*meso*-**8**) (0.50 g, 1.6 mmol) in benzene (15 mL) was added dropwise over 10 min. During this time the reaction mixture became cloudy, and a white precipitate formed. After 4 h the mixture was filtered, and hexane was added. The organic layer was washed with water (3 × 10 mL) and dried over sodium sulfate. The organic solvents were removed, and the sample was dried in vacuo. The yield was 1.69 g (100%) of a white powder with a melting point of 56−64 °C dec. ^{1}H NMR ($CDCl_3$, ppm): 1.28 (s, 36H), 1.43 (m, 4H), 1.55 (s, 6H), 2.25−2.65 (m, 12H), 4.01 (t, J = 5.8 Hz, 4H), 7.15 (m, 26H). ^{13}C NMR ($CDCl_3$, ppm): 23.6, 25.3, 29.2, 31.3, 33.2, 34.4, 36.6, 55.4, 65.6, 71.7, 117.6, 124.6, 127.7, 128.7, 129.0, 144.0, 147.0, 148.0, 171.0 (theory 20, found 19). Anal. Calcd: C, 80.56; H, 8.26. Found: C, 80.71; H, 8.66.

***meso*-*p*-[Tris(*p-tert*-butylphenyl)methyl]phenyl 4,4′-Azobis[4-cyanopentanoate] (*meso*-10).** A solution of *meso*-4,4′-azobis[4-cyanopentanoic acid] (*meso*-**7**) (0.53 g, 1.9 mmol), *N*,*N*′-dicyclohexylcarbodiimide (1.23 g, 5.96 mmol), tris(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane (**6**) (2.00 g, 3.97 mmol), and a catalytic amount of 4-pyrrolidinopyridine in THF (25 mL) was allowed to stir at room temperature until esterification was complete (3 h). The *N*,*N*′-dicyclohexylurea was filtered, and the solvent was removed in vacuo. The off-white residue (2.37 g, 100%) was purified by column chromatography on silica gel with hexane−ethyl acetate (9:1) as eluent. Mp: 230−236 °C. ^{1}H NMR ($CDCl_3$, ppm): 1.30 (s, 27H), 1.74 (s, 3H), 2.5−2.9 (m, 4H), 6.97 (d, J = 9 Hz, 2H), 7.07 (d, J = 8 Hz, 4H), 7.24 (m, 10H). ^{13}CNMR ($CDCl_3$, ppm): 23.96, 29.51, 31.50, 33.23, 34.43, 63.49, 71.94, 117.65, 119.96, 124.28, 130.84, 132.38, 143.76, 145.30, 148.38, 148.61, 170.00 (theory 17, found 17). Anal. Calcd: C, 82.39; H, 8.04. Found: C, 81.97; H, 8.18.

***dl*- and *meso*-*p*-[Tris(*p-tert*-butylphenyl)methyl]phenyl 4,4′-Azobis[4-cyanopentanoate] (10).** In a 100-mL 1-neck flask equipped with a condenser, a magnetic stirring bar, and a N_2 bubbler were placed 4,4′-azobis[4-cyanopentanoic acid] (**7**) (1.00 g, 3.57 mmol), tris(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane (**6**) (5.40 g, 10.7 mmol), *N*,*N*′-dicyclohexylcarbodiimide (2.90 g, 14.1 mmol), (dimethylamino)pyridine (catalytic amount), and dry THF (50 mL). The mixture was stirred at room temperature for 6 h. The mixture was filtered, and the solvent was evaporated under reduced pressure. The desired product was isolated by column chromatography (silica gel, CH_2Cl_2 eluent). The white solid was recrystallized from a mixture of toluene and hexane (3:2 by vol). The yield was 1.30 g (29%, *dl*/*meso* = 0.78). Mp: 206−217 °C. ^{1}H NMR ($CDCl_3$, ppm): 1.29 (s, 30.3H), 1.23 (s, 23.7H), 1.73 (s, 3.4H), 1.79 (s, 2.6H), 2.45−2.85 (m, 8H), 6.96 (d, J = 9.2 Hz, 4H), 7.07 (dd, J = 8.4, 2 Hz, 8H), 7.18−7.26 (m, 20H). ^{13}C NMR ($CDCl_3$, ppm): 23.83, 24.11, 29.28, 29.34, 31.37, 33.04, 33.11, 43.30, 63.36, 71.82, 71.93, 117.43, 117.53, 119.83, 124.16, 130.70, 132.26, 143.64, 145.18, 145.21, 148.20, 148.22, 148.48, 148.51, 169.81, 169.88 (theory 26 for two diastereomers, found 26). Anal. Calcd: C, 82.39; H, 8.04. Found: C, 82.00; H, 8.11.

Decomposition Study of *dl*- and *meso*-4-[Tris(*p-tert*-butylphenyl)methyl]phenyl 4,4′-Azobis[4-cyanopentanoate] (10). 4-[Tris(*p-tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (**10**) (7.6 mg) was added to toluene (5 mL, deoxygenated with N_2 bubbling before use) in a 25-mL flask equipped with a magnetic stirring bar and a N_2 bubbler. The flask was placed in an oil bath preheated to 85 °C. Small aliquots were taken out after 2 and 6 h of stirring. The samples were dried in vacuo at room temperature before ^{1}H NMR analysis.

Polymerization of Styrene Using *meso*-4,4-Bis(*p-tert*-butylphenyl)-4-phenylbutyl 4,4′-Azobis[4-cyanopentanoate] (9). Styrene was passed through a column of basic alumina and then deoxygenated with nitrogen gas for 10 min before use. Toluene was deoxygenated with nitrogen for 10 min before use. In a 15-mL polymerization tube equipped with a magnetic stirring bar were placed styrene (0.45 g, 4.3 mmol), 4,4-bis(*p-tert*-butylphenyl)-4-phenylbutyl 4,4′-azobis[4-cyanopentanoate] (0.059 g, 5.5×10^{-2} mmol), and toluene (1.0 mL). The mixture was immersed in an oil bath preheated to 100 °C and allowed to react for 20 h. The polymerization tube was opened, CH_2Cl_2 was added, and the solution was poured into hexane. The precipitate was filtered, dissolved in CH_2Cl_2, and precipitated from hexane again. The third precipitation was done from methanol.

Polymerization of Styrene Using *dl*- and *meso*-*p*-[Tris(*p-tert*-butylphenyl)methyl]phenyl 4,4′-Azobis[4-cyanopentanoate] (10). Styrene was washed with dilute aqueous NaOH (5%) to remove the inhibitor (*tert*-butylcatechol) followed by water, dried over anhydrous $MgSO_4$, and vacuum-distilled at room temperature with a receiver flask in a dry ice bath. Styrene (0.50 g, 4.8 mmol), *dl*-and *meso*-4-[tris(*p-tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (**10**) (*dl*/meso = 0.78) (0.060 g, 4.8×10^{-2} mmol), and toluene (4.0 g) were placed in a 50-mL round-bottomed flask fitted with a joint and Teflon valve. A small magnetic stirring bar was put into the reaction mixture. The reaction mixture was subjected to three cycles of freeze−pump−thaw processes on a vacuum line to remove oxygen from the reaction mixture. The flask was placed in an oil bath preheated to 85 °C. After 3 days of reaction, the reaction mixture was poured into vigorously stirred ethanol (250 mL). The white precipitate was filtered, dried, and then dissolved in CH_2Cl_2 (10 mL) and poured into ethanol (250 mL) again. The precipitate was filtered, and such precipitation was done once more. The final product was dried in vacuo at room temperature.

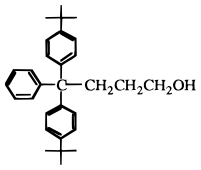
Poly(styrene−rotaxa-crown ether) (11). Styrene (0.50 g, 4.8 mmol), *dl*- and *meso*-4-[tris(*p-tert*-butylphenyl)methyl]-phenyl 4,4′-azobis[4-cyanopentanoate] (**10**) (*dl*/meso = 0.78) (0.060 g, 4.8×10^{-2} mmol), toluene (2.0 g), and a mixture of

crown ethers[23] (**12**) (2.0 g) (M_n = 3400, determined by GPC with PS standards) were placed in a 50-mL round-bottomed flask fitted with a joint and Teflon valve. A small magnetic stirring bar was placed in the flask, and the mixture was subjected to three freeze−pump−thaw processes on a vacuum line to remove oxygen from the mixture. The reaction mixture was placed in a preheated oil bath. The mixture was stirred at 95 °C for 3 days. The mixture was poured into methanol (250 mL), and the precipitate was filtered. Two more reprecipitations were done, and the final precipitate was dried in vacuo at room temperature; 0.17 g (yield 34%) of white powder was obtained. M_n determined by GPC (Figure 7, PS standards, $CHCl_3$, differential viscometer detector) was 23.4K and polydispersity (Pd) was 1.3.

A control experiment was carried out using 18c6 (Aldrich, 99%) instead of the crown ethers (**12**) with the same procedure (same masses). After two reprecipitations into excess methanol, according to the ^{1}H NMR spectrum in $CDCl_3$ the isolated polymer was found to contain 0.2 mass % of the crown ether species.

Results and Discussion

The blocking groups used in this work were triarylmethyl derivatives: 4,4-bis(*p-tert*-butylphenyl)-4-phenylbutanol (**5**) and tris(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane (**6**).[6]



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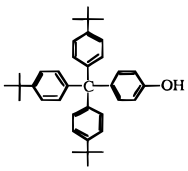

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The introduction of the blocking groups into the azo compound to synthesize the BG/inits was achieved by two methods. In the first method we sought to convert 4,4′-azobis[4-cyanopentanoic acid] (**7**) into its acid chloride for reaction with a hydroxyl-functionalized blocking group. Smith had reported the synthesis of 4,4′-azobis-[4-cyanopentanoyl chloride] (**8**) by treating 4,4′-azobis-[4-cyanopentanoic acid] (**7**) with phosphorous pentachloride.[9] However, he only reported the melting point, which was 93−95 °C. No yield or spectral data were given. While numerous papers have reported the use of derivatives of **8** to initiate radical polymerizations,[11,12] preparing this compound was not a trivial task. Smith's method was attempted several times, but complete conversion was never achieved. We believe that this was due to the difference in reactivity between the diastereomers. In the patent of 1973 for preparing various azo compounds containing acyl functionalities, Sheppard reported that compound **7** could be separated into two isomers by repeated recrystallizations from ethanol and ethyl acetate.[10] The less soluble isomer, which Sheppard called the *trans* isomer, melted at 141−145 °C, and the more soluble *cis* isomer, according to Sheppard, melted at 125−127 °C. Also, this patent stated that before quantitative conversion of the acid **7** into the acid chloride **8** could be accomplished, the two isomers had to be separated.

However, the structural assignment of the isomers was examined, and we came to believe that compound **7** was not a mixture of *cis* and *trans* isomers but a mixture of the enantiomers and *meso* compound. The ^{1}H NMR spectrum (acetone-d_6) of **7** showed the α-CH_3 proton peaks at 1.73 and 1.79 ppm in about a 1:1 ratio (Figure 1). Two starred carbon atoms (*) in the structure of compound **7** are chiral; it may have the configuration of *R,R*, *S,S*, or *meso* diastereomers in both the *cis* and *trans* isomers.

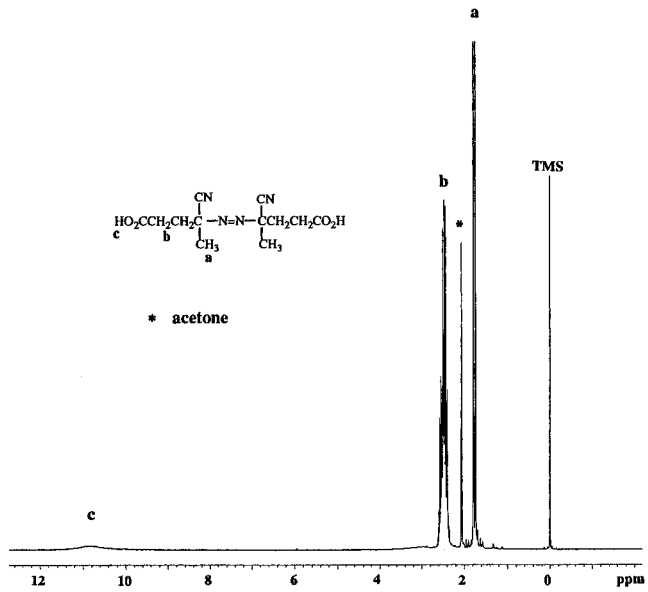
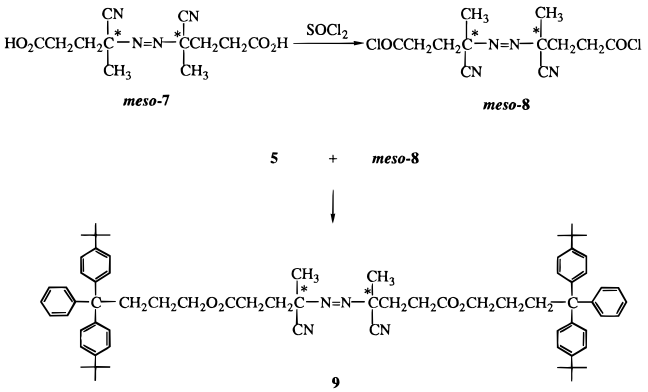


Figure 1. ^{1}H NMR spectrum of 4,4′-azobis[4-cyanopentanoic acid] (**7**) (acetone-d_6, 400 MHz).



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Therefore, if compound **7** is a mixture of *trans* and *cis* isomers, the α-CH_3 protons must give more than two peaks in the ^{1}H NMR spectrum, more complex peaks due to *trans*−*cis* isomerism as well as diastereoisomerism. The activation enthalpies for the interconversion of various azo compounds between *cis* and *trans* forms usually lie in the range of 18−40 kcal/mol, which is not high enough to prevent the interconversion even at room temperature.[13] As a result *cis* isomers convert into the *trans* isomers even at room temperature, and the azo compounds exist in the *trans* forms which are more stable than *cis* forms by usually 10−30 kcal/mol.[13] If the azo compound **7** is a mixture of diastereomers which are *trans* compounds, the number of the α-CH_3 proton peaks is supposed to be two, one of which comes from *dl* isomers and the other comes from the *meso* diastereomer, as observed (Figure 1). Diastereomers have different properties such as melting point and solubility.[14] Especially, tartaric acid shows big differences in melting point and solubility.[15] *dl*-Tartaric acid has a higher melting point (206 °C) and lower solubility compared with *meso*-tartaric acid (mp 140 °C). Thus, we assigned the less soluble isomer with the higher melting point (141−143 °C) as the *dl* isomer and the other (mp 125−127 °C) as the *meso* isomer. In the ^{1}H NMR spectrum, the peak at 1.79 ppm came from the *dl* isomer and the peak at 1.73 ppm is from the *meso* compound.

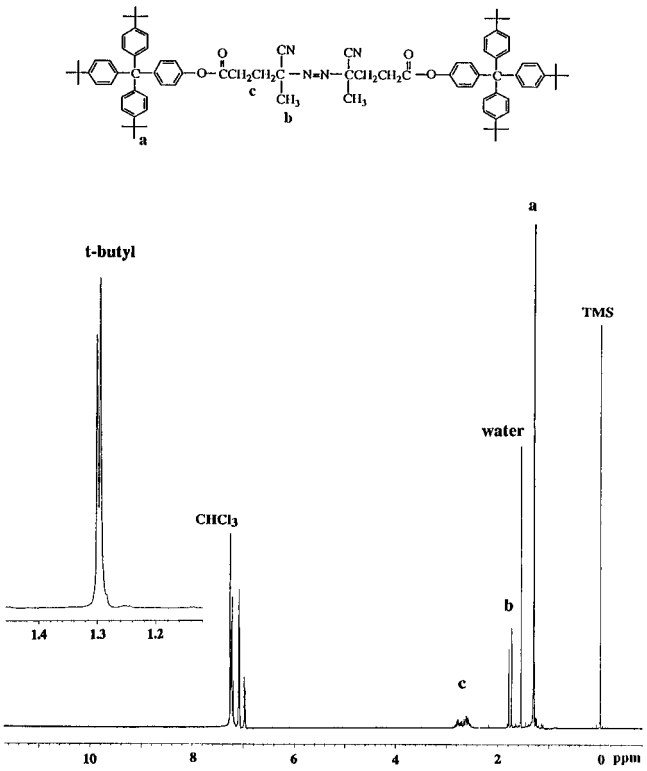


Figure 2. ^{1}H NMR spectrum of *dl*- and *meso*-4-[tris(*p*-*tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (**10**, BG/init **II**) ($CDCl_3$, 400 MHz).

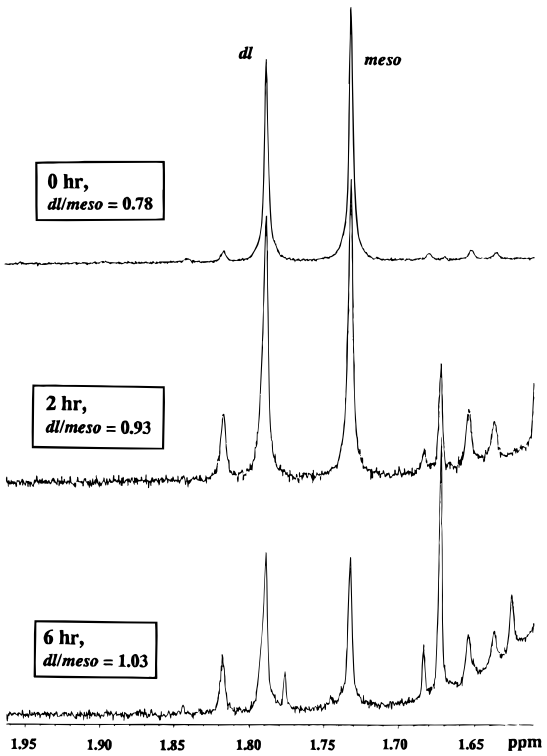
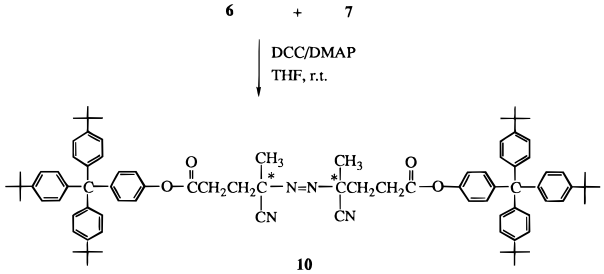


Figure 3. Relative decomposition rates of *dl*- and *meso*-4-[tris(*p*-*tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (**10**, BG/init **II**) in toluene at 85 °C ($CDCl_3$, 400 MHz).

Using the more soluble isomer (*meso*-**7**), quantitative conversion to its acid chloride (*meso*-**8**) was accomplished by heating with excess thionyl chloride at 120 °C for 10 min. On the other hand, the *dl* isomer needed to be exposed to a larger excess of refluxing thionyl chloride for 1 h at 100 °C, and still there existed some of the unreacted acid. The reaction of **5** with *meso*-**8** afforded **9** (BG/init **I**) in quantitative yield.

The second method for connecting the blocking group to the azo compound **7** was by using dicyclohexylcarbodiimide (DCC) coupling,[16] which proved to be a better way than the acid chloride method. In the reaction, *meso*-4,4′-azobis[4-cyanopentanoic acid] (*meso*-**7**) reacted with tris(*p*-*tert*-butylphenyl)(4-hydroxyphenyl)methane (**6**) at room temperature to give *meso*-4,4-[tris(*p*-*tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (*meso*-**10**, *meso*-BG/init **II**). A catalytic amount of 4-pyrrolidinopyridine or 4-(dimethylamino)pyridine was used to augment the reaction. This direct coupling method was milder than the acid chloride route, and the yield was also good.

The yield, however, was lower than 30% when 4,4′-azobis[4-cyanopentanoic acid] (**7**) as received was used instead of the isolated *meso* isomer (*meso*-**7**). It is believed that the low yield was related to the low reactivity of *dl* isomers as previously mentioned. The ^{1}H NMR spectrum in $CDCl_3$ demonstrated that when **7** was used as received the product 4-[tris(*p*-*tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (**10**, BG/init **II**) was a mixture of the diastereomers; in Figure 2 the *tert*-butyl and α-CH_3 each show two peaks. According to the peak integrations the ratio of the two isomers was *dl*/*meso* = 0.78. This ratio also indicated that the reactivity of the *meso* isomer was higher than that of the *dl* isomer. Also, in the ^{13}C NMR spectrum of **10** in $CDCl_3$ 26 lines were found, which was different from the ^{13}C NMR spectrum of *meso*-4,4′-[tris(*p*-*tert*-butylphenyl)methyl]phenyl 4,4′-azobis[4-cyanopentanoate] (*meso*-**10**) which showed 17 lines as expected. Mixed **10** melted between 206 and 217 °C, which was broader and lower as compared with the melting point of the *meso* compound (*meso*-**10**) which was 230−236 °C. This result was as expected because the mixture of the diastereomers must melt at a lower and broader temperature range than each of the pure stereoisomers.



Because the BG/init **II** (**10**) was a mixture of diastereomers, instead of isolating them from each other, the relative thermal decomposition rates of the isomers were investigated in toluene at 85 °C. At the end of 2- and 6-h heating periods, small aliquots were taken and analyzed by ^{1}H NMR spectroscopy. As shown in Figure 3, the rates of disappearance of peaks at 1.73 ppm (*meso*) and 1.79 ppm (*dl*) were not so different. However, the peak at 1.73 ppm (*meso*) was found to reduce slightly faster than the peak at 1.79 ppm (*dl*). This might be due to the difference in strain energy. A computer molecular simulation (Cerius^2)[8] indicated that the total energy of the *meso* isomer was larger than that of the *d* or *l* isomer by 3 kcal/mol: 258.74 vs 255.70 kcal/mol. Although the difference is small the result demonstrated that the *meso* isomer would decompose faster than *dl* isomers. The thermal decomposition rates of *dl* and *meso* stereoisomers of a few azo compounds have been reported to be approximately the same.[13]

Table 1. Polymerization[a] of Styrene with BG/Inits and AIBN[b]

sample	initiator	initiator conctn (mmol × 10^2)	styrene conctn (mmol)	isolated yield (%)	M_n[c] (kg/mol)
1	**9**	5.5	4.3	70	15.1
2	**9**	10.7	4.3	63	10.5
3	**9**	15.7	4.3	59	8.3
4	**9**	22.9	4.3	79	7.4
5	**10**	2.5	4.9	64	18.5
6	**10**	5.0	5.0	59	15.2
7	**10**	10.0	4.9	68	9.5
8	**10**	5.0	4.9	64	13.4
9	AIBN	3.5	4.8	95	17.2
10	AIBN	6.1	4.8	90	10.6
11	AIBN	12.0	4.8	85	6.2
12	AIBN	23.6	4.8	83	2.2

[a] Polymerizations were done in toluene (1 mL) at 100 °C for 20 h for samples 1−4 and 9−12 and in toluene (4 mL) at 85 °C for 3 days for samples 5−8. [b] Recrystallized from ethanol. [c] Measured by GPC (THF for samples 1−4 and 9−12, $CHCl_3$ for samples 5−8, PS standards).

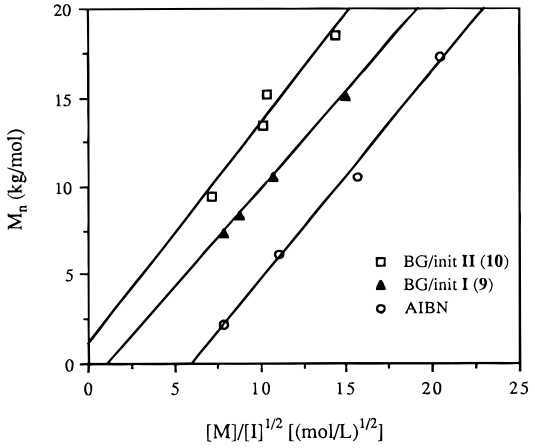


Figure 4. M_n of polystyrene vs [M]/[I]$^{1/2}$ using AIBN, BG/init **I** (**9**), or BG/init **II** (**10**).

Characterization of BG/Init: Polymerization of Styrene. In order to investigate the initiation of free radical polymerizations and blocking abilities of the two synthesized BG/inits, polymerizations of styrene were carried out using the BG/inits **I** (**9**) and **II** (**10**).

Table 1 and Figure 4 show the results of the polymerization of styrene using BG/inits **I** (**9**) and **II** (**10**) and AIBN. In order to remove the unreacted initiator, the reaction mixtures were precipitated into excess methanol (samples 9−12). For the other samples, hexane and ethanol were used for precipitations because methanol was not a good solvent for the BG/inits **I** and **II**. Thus, for samples 1−4, the mixtures were precipitated into excess hexane twice followed by once into methanol. Samples 5−8 were precipitated into excess ethanol three times to remove the unreacted BG/init **II**.

Table 1 shows that as the amount of initiator increased the molecular weight of the polymer obtained decreased, as expected. The polymerization conditions for the BG/init **II** were different from the other two; the yields of polymerization initiated by the BG/inits were generally lower than by AIBN. The plots of M_n (number-average molecular weight) vs [M]/[initiator]$^{1/2}$ (concentration of monomer/inverse square root of initiator concentration) (Figure 4) show linear relationships for each initiator, which means that the BG/inits **I** (**9**) and **II** (**10**) are well-behaved free radical initiators. It is noted that the slopes of the lines are similar to each other.

The decomposition rates of azo compounds are known to primarily depend on the functional groups on the α-carbon from the azo unit.[17] The structural strain plays a role in decomposition rates too.[17−19] The carbonyl group is not likely to affect the decomposition rates. It was reported that 4,4′-azobis[4-cyanopentanoic acid] (**7**) showed a decomposition rate similar to AIBN.[20] It is, however, believed that the decomposition rates of the BG/inits **I** (**9**) and **II** (**10**) are greater to some extent than AIBN due to the bulky groups.

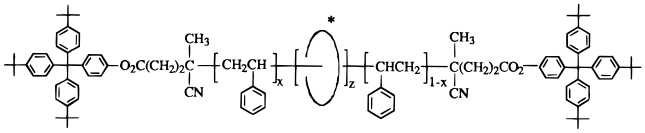
Another consideration is initiation efficiency *f*. The initiation efficiency is known to depend on viscosity of solvent and polymerization medium. The initiation efficiency decreases with viscosity because as viscosity increases the diffusion rate of the primary radicals from the solvent cage decreases.[20,21] Therefore, the initiation efficiencies of the BG/inits **I** (**9**) and **II** (**10**) are believed to be smaller than that of AIBN because of the attached bulky blocking groups. Due to the bulkiness, the rate of diffusion of the primary radicals of the BG/inits **I** (**9**) and **II** (**10**) from the solvent cage would be slower compared to AIBN. Therefore, it is likely that the two factors bearing on the decomposition rate, which are strain and solvent cage effects, compensated each other and resulted in the decomposition rates of the BG/inits **I** (**9**) and **II** (**10**) similar to AIBN. The lower polymerization yields of BG/inits seem to be related to the lower initiator efficiencies of the BG/inits.

It is to be noted that the intercept of the line for AIBN is negative, but within experimental error this is not the case for those of BG/inits in Figure 4. This suggested that the chain transfer constants to the initiators are different. As compared to AIBN, the BG/inits are believed to have smaller chain transfer constants because of a steric hindrance due to the bulky blocking groups.

Along with the initiation ability, the blocking efficiency of the BG/inits is an important factor for the synthesis of polyrotaxanes. Polystyrene is known to terminate almost exclusively *via* radical coupling rather than disproportionation.[20,22] In the synthesis of polyrotaxanes, termination by coupling affords completely end-blocked polyrotaxanes.

The blocking efficiencies of the BG/inits in the polymerization of styrene could be determined by comparison of the end-group analyses from the ^{1}H NMR spectra (Figure 5) and the molecular weights from the GPC of the resultant polymers. Althought the end-group analysis based on the peak integrations of *tert*-butyl and aromatic protons was not easy due to peak overlap, the blocking efficiencies were found to be 100% within an error range of ±10%.

Synthesis of a Poly(styrene−rotaxa-crown ether). A poly(styrene−rotaxa-crown ether) (**11**) was prepared by free radical polymerization of styrene in the presence of crown ethers using BG/init **II**. The mixture of crown ethers (**12**) did not contain linear impurities.[23]



11

12

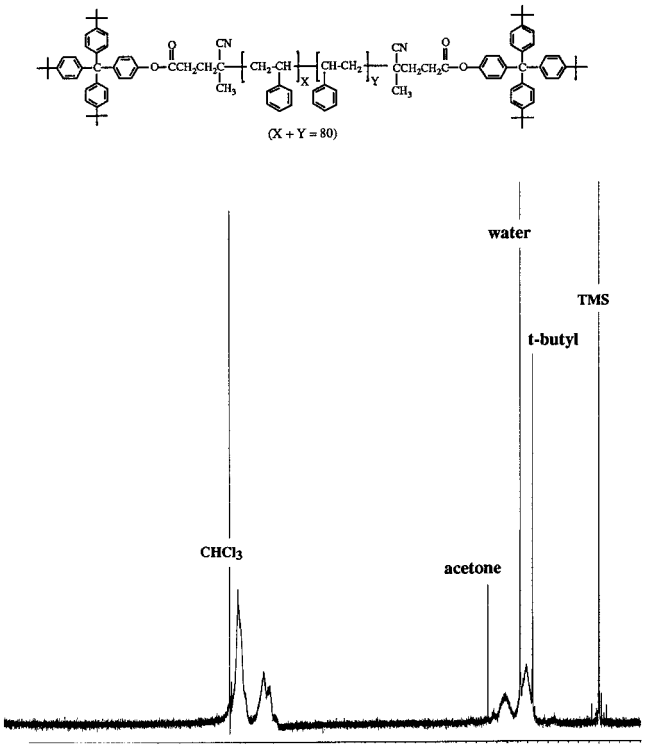


Figure 5. ^{1}H NMR spectrum of polystyrene initiated by BG/init **II** (**10**) sample 11) ($CDCl_3$, 400 MHz).

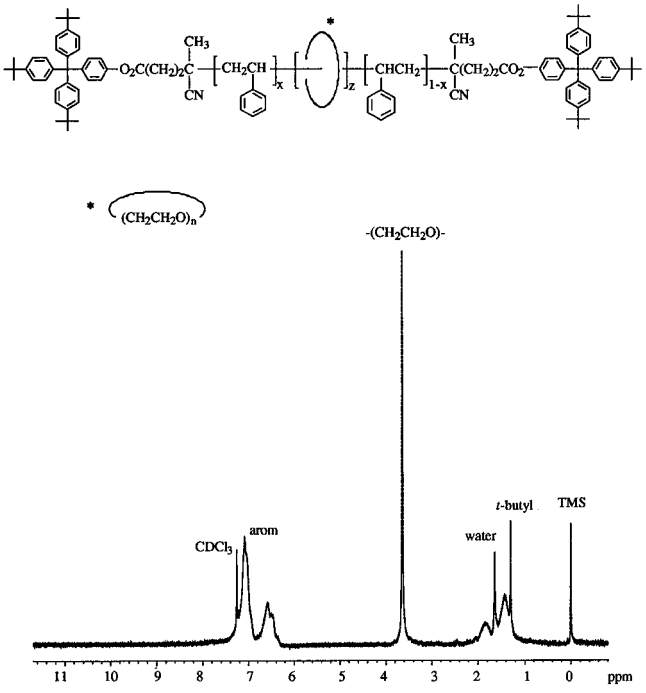


Figure 6. ^{1}H NMR spectrum of poly(styrene−rotaxa-crown ether) (**11**) ($CDCl_3$, 400 MHz).

Due to the incompatibility between polystyrene and crown ethers, toluene was employed as a cosolvent to maintain a homogeneous reaction mixture throughout the polymerization reaction. Removal of unthreaded crown ethers was achieved by repeated precipitations of the crude product into excess methanol until a constant mass percentage of crown ethers was observed in the precipitate, which was determined by ^{1}H NMR spectroscopy.

Figure 6 is the ^{1}H NMR spectrum of the purified polyrotaxane **11**, from which the threaded crown ether content was determined to be 21 mass % by the ratio of the peak integrations of crown ether and aromatic protons. For further verification of the absence of the free crown ethers, GPC analyses were carried out. Figure 7 shows GPC traces for three samples: (a) crown ethers (**12**), (b) a physical blend of the crown ethers (**12**) and a model polystyrene (M_n = 35.5K, Pd = 2.4), and (c) poly(styrene−rotaxa-crown) (**11**). Figure 7c indicated the absence of the free crown ethers in the final product (**11**).

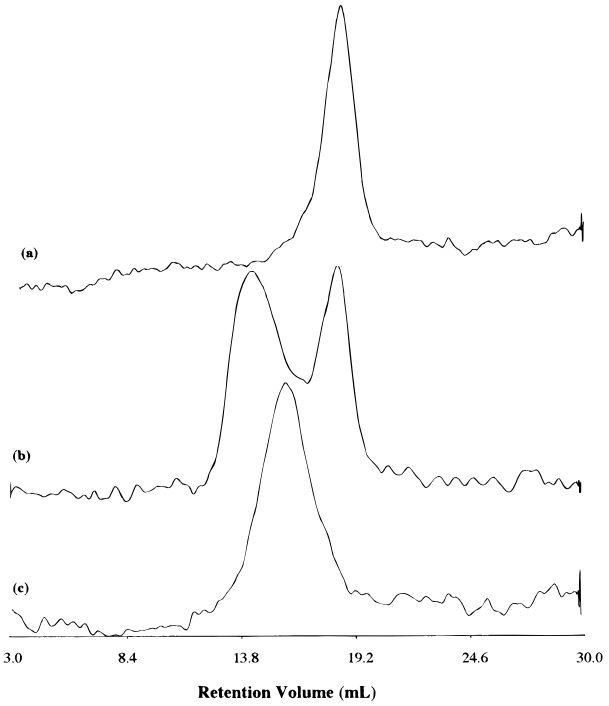


Figure 7. GPC traces of (a) crown ethers (**12**), (b) a blend of polystyrene (M_n = 35.5K, Pd = 2.4) and 50 mass % crown ethers (**12**), and (c) poly(styrene−rotaxa-crown ether) (**11**) (M_n = 23.4K, Pd = 1.3) (solvent $CHCl_3$, universal calibration).

As a control experiment, the polymerization of styrene using BG/init **II** was carried out under the same reaction conditions in the presence of 18-crown-6, whose cavity is too small to be threaded by polystyrene chains. After removal of free 18-crown-6 by two reprecipitations into excess methanol, it was found that 0.2 mass % of the crown species was incorporated in the final polymer according to the ^{1}H NMR spectrum. Thus, chain transfer to the crown ether was found to be negligible.

Conclusions

Two new BG/inits, which contained azo units and bulky triarylmethyl groups at both ends, were synthesized. In the synthesis of the BG/inits, two methods were used; one was the acid chloride method, and the other was the DCC coupling method. 4,4-Bis(*p-tert*-butylphenyl)-4-phenylbutyl 4,4′-azobis[4-cyanopentanoate] (**9**, BG/init **I**) was prepared by the acid chloride method in which 4,4′-azobis[4-cyanopentanoyl chloride] (*meso*-**8**) was reacted with 4,4-bis(*p-tert*-butylphenyl)-4-phenylbutanol (**5**). 4-[Tris(*p-tert*-butylphenyl)methyl]-phenyl 4,4′-azobis[4-cyanopentanoate] (**10**, BG/init **II**) was synthesized by the reaction of 4,4′-azobis[4-cyanopentanoic acid] (**7**) with tris(*p-tert*-butylphenyl)(4-hydroxyphenyl)methane (**6**) using DCC coupling.

The results of the polymerization of styrene using the two BG/inits demonstrated that the BG/inits were good free radical initiators, affording end-blocked polystyrenes. Indeed, a polymerization of styrene using BG/

init **II** in the presence of crown ethers (**12**) produced poly(styrene−rotaxa-crown ether) (**11**) which contained 21 mass % of the cyclic species. Thus, the two BG/inits can be used for the synthesis of polyrotaxanes whose linear species are made from free radical polymerizations of olefinic monomers.

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(23) This material was prepared by the procedure we reported for the synthesis of 42-crown-14 (Gibson, H. W.; Bheda, M. C.; Engen, P. T.; Shen, Y. X.; Sze, J.; Zhang, H.; Gibson, M. D.; Delaviz, Y.; Lee, S.-H.; Liu, S.; Wang, F.; Nagvekar, D.; Rancourt, J.; Taylor, L. T. *J. Org. Chem.*, **1994**, *59*, 2186). Subsequent detailed GPC study in collaboration with Prof. Colin Booth and colleagues at the University of Manchester (U.K.) showed it to contain rings with up to 400 or so atoms, i.e., ∼130 repeat units. MALDI-TOF MS indicates that only rings of multiples of seven ethyleneoxy units are present; the largest ring detected was $(CH_2CH_2O)_n$, $n = 142$ with $M = 6248$; the largest signal corresponded to $n = 30$, $M = 1320$. This latter value is viewed as more reliable than the GPC value. Of course the blocking groups will not prevent the dethreading of rings larger than ca. 42 atoms, $n = 14$, so presumably the retained rings are the smaller ones, and thus the value of z/x is not known.

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