

# Block Copolymers Derived from 2,2'-Azobis(2-cyanopropanol). I. Synthesis of Poly(urethane-*block*-methyl methacrylate) and Poly(urethane-*block*-styrene)

TALAL CHEIKHALARD, VALERIE MASSARDIER, LAN TIGHZERT,\* JEAN PIERRE PASCAULT

Laboratoire des Matériaux Macromoléculaires, UMR 5627, Institut National des Sciences Appliquées de Lyon, Bât. 403, 20, avenue Albert Einstein, 69621 Villeurbanne Cedex, France

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**ABSTRACT:** Block copolymers with polyester-urethane and polymethyl methacrylate (PMMA) or polystyrene (PS) sequences were obtained by the use of polyester- or polyether-urethane macroazo initiators (PUMAI). PUMAI with a well-defined number of azo groups per chain were prepared via a two-stage reaction procedure using 2,2'-azobis(2-cyanopropanol) (ACP), 4,4'-methylene diphenyl diisocyanate (MDI) and  $\alpha$ ,  $\omega$ -hydroxy polycaprolactone (PCL). The characteristics of the obtained block copolymers depend on the reaction conditions, and a yield of 98% was obtained for a P(U-*b*-MMA) synthesized with a ratio of macroazo initiator to monomer equal to 1/400. In similar conditions, copolymerization of styrene was more difficult, and the maximum block copolymer yield obtained in this work was only of 37% for a ratio of macroazo initiator to monomer equal to 1/150. Combination of different analyses Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ), and size exclusion chromatography (SEC) carried out on both crude and fractionated copolymers showed this kind of synthesis yielding di- and triblock copolymers and only a little amount of PU homopolymer. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 613–627, 1998

**Key words:** polyurethane; macroazo initiator; block copolymers; radical polymerization; fractionation

## INTRODUCTION

In recent years, there has been growing interest in the synthesis of new materials with specific properties. Block copolymers that provide a combination of different properties are the most suitable materials for various uses in bulk or as additives, such as thermoplastic elastomers, modifiers for homopolymers, or compatibilizers for

polymer blends. Classical methods using a single type of propagating species such as anionic polymerization are limited to certain types of monomers. Recent developments for “living” radical polymerization lead to well-defined homopolymers and copolymers of different monomers such as styrene, acrylates, etc.,<sup>1</sup> and also can be used in the polymerization of macromonomers to yield graft copolymers, or to prepare well-defined block copolymers.<sup>2</sup>

In the last 20 years, many studies<sup>3–7</sup> were carried out with macroazo initiators (MAI) for preparing various block<sup>8–10</sup> and graft<sup>11,12</sup> copolymers via conventional operations of radical polymerization. This way of synthesis is very flexible<sup>13–16</sup> and allows combination of hard and soft seg-

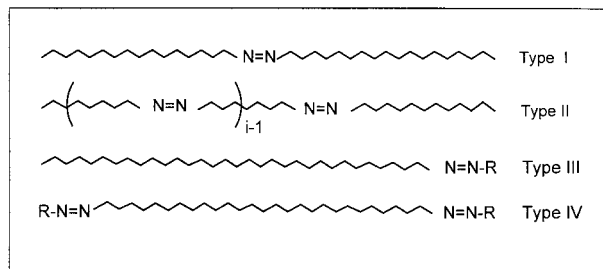
Correspondence to: V. Massardier.

\*Present address: Université des Sciences et Technologies de Lille, Laboratoire de Chimie Macromoléculaire, URA CNRS 351, Bât. C6, 59655 Villeneuve D'Asq Cedex.

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**Scheme 1** Different types of macroazo initiators.<sup>24</sup>

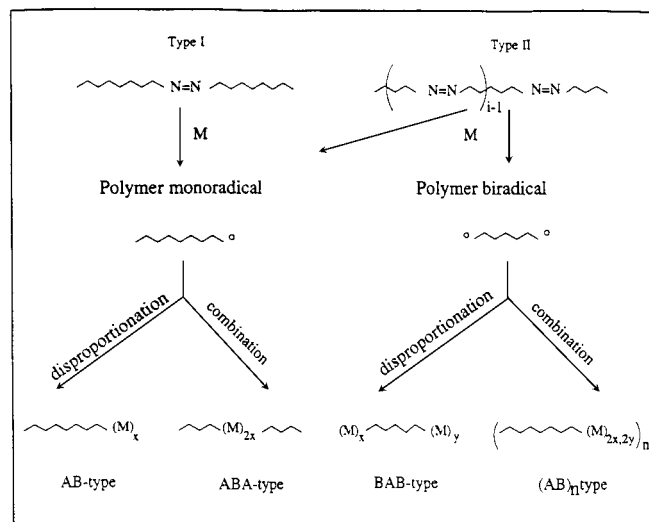
ments, or even hydrophilic and hydrophobic segments.<sup>13</sup> This new kind of initiators also enables researchers to combine different kinds of polymerization reactions. Indeed, MAI can be synthesized using azo initiators having both condensation functions<sup>17,18</sup> or ionic initiation<sup>19–22</sup> ability and a scissile azo group (N=N) for radical polymerization. They can be used in one- or two-stage processes for radical polymerization. In one-stage processes, structures are of the form  $(RA_mX)_n$ , where  $A_m$  is a polymer chain,  $R$  an alkyl group or alkyl group having a functional group such as alcohol, isocyanate, etc., and  $X$  an active site for scission, whereas for two-stage routes they are  $(RX)_n$ . For two-stage radical polymerization, recent studies<sup>23</sup> have demonstrated the interest of MAI with dual decomposition temperature due to two kinds of azo groups.

For molecular design of block copolymers it is essential to synthesize the macroazo initiator having a desired small number of —N=N— linkages in the main chain because the azo concentration is an important factor for both the block copolymerization stage and the segment lengths in the block copolymer. The macroazo initiators can be classified according to the location of the azo group. They can be distinguished as follows<sup>24</sup>:

The polymer chains with exactly one azo group in the chain are of type I. Type II contains several azo units in the main chain. Types III and IV contain one or two azo groups, respectively, at the end of the chain,  $R$  being an alkyl group or alkyl group having a functional group such as alcohol, isocyanate, etc. The labile azo group along the polymer backbone is cleaved thermally to yield a polymer radical (type I) or a polymer biradical (type II), which, in the presence of vinyl monomer, initiates radical chain polymerization. Scheme 2 shows idealized examples of block copolymerization using macroazo initiators involving no transfer reaction during the chain polymerization process. According to Scheme 2, polymer chains with one inside azo group (type I) yields AB

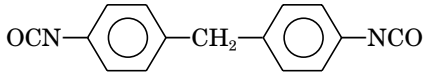
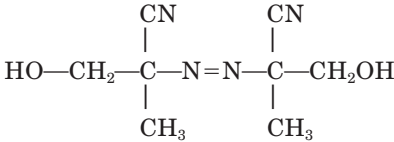
or ABA block copolymers, depending on the preferred type of termination reaction (disproportionation or combination). In the case of several azo groups distributed along the polymer chain (type II) biradical can be obtained, yielding, therefore, in the presence of a vinyl monomer,  $(AB)_n$  and BAB-type structures, depending on the type of termination reaction. One azo group at the end of the chain yields not only a polymer radical (type III) or biradical (type IV) but also a monomer radical  $R^\bullet$ , which, in the presence of a vinyl monomer yields polyvinyl homopolymers. So, the types III and IV are less convenient than I and II for obtaining block copolymers in a quantitative way (Scheme 2).

The aim of this study is the synthesis of block copolymers based on polyurethane and polymethyl methacrylate (PMMA) or polystyrene (PS) sequences using well-defined PUMAI of type I (or II) as macroazo initiators. First, the synthesis of several kinds of PUMAI based on 2,2'-azobis(2-cyanopropanol) ACP, 4,4'-methylene diphenyl diisocyanate MDI, and  $\alpha,\omega$  hydroxy polycaprolactone PCL ( $M_n = 550$  and  $1000$  g/mol) was performed in a two-stage polymerization, similar to the procedure described in our previous article.<sup>25</sup> The reactivity ratio  $\lambda$  of the substituted OH group of ACP to the initial one, when reacted with paratolyl isocyanate (*p*-TI), in 2-butanone at 35°C with dibutyltin dilaurate (SnDBDL) as a catalyst, was found to be equal to 1.6. The characterization, the decomposition, and the thermal behavior of ACP compared to other azo initiators and to azo and macro azo initiators based on ACP were also investigated in bulk and in solution.<sup>26</sup>



**Scheme 2** Synthesis of block copolymers using type I and type II macroazo initiators.<sup>24</sup>

**Table I** Raw Materials Used for PUMAI Synthesis

Designation	Chemical Formula	Molar Mass (g/mol)
MDI		250
ACP		196
PCL	$\text{H}-\{ \text{O}-[ \text{---}(\text{CH}_2)_5\text{---CO} ]_n\text{---O} \}_2\text{---R}$	550 and 1000

The kinetic parameters of a typical PUMAI were determined. PUMAI was then used in solution and in the presence of methyl methacrylate (MMA) or styrene (S) to initiate a radical polymerization. The separation of eventual homopolymers from block copolymers was performed by fractionation of crude block copolymers. The selection of nonsolvent/solvent systems was determined by a turbidimetric titration. The determination of the relative proportions of PU and PMMA or PS sequences were made using SEC and  $^1\text{H-NMR}$  analyses. PUMAI could also be used as antishrinkage agents and macro azo initiators for the crosslinking of unsaturated polyesters. P(U-*b*-S) block copolymers prepared could be used as compatibilizers for thermoset/thermoplastic systems such as epoxy-amine/polypropylene oxide.

## EXPERIMENTAL

### Materials

4,4'-Methylene diphenyl diisocyanate (MDI) (pure MDI Bayer) (Table I) was used without further purification.  $\alpha,\omega$ -Hydroxy polycaprolactone (PCL)  $\bar{M}_n = 550$  and 1000 g/mol (Interox Chemical) were dried under reduced pressure for 3 h at 100°C before use. 2,2'-Azobis(2-cyanopropanol) (ACP) (Wako Chemicals) was washed by swirling in diethyl ether for 3 h at 25°C, then filtered, and finally dried under reduced pressure for 2 days. Methyl methacrylate and styrene (Aldrich) were purified twice by distillation. Dibutyltin dilaurate (SnDBDL), anhydrous 2-butanone, dibutylamine (DBA), and hydroquinone (HQ) (Aldrich) were used as received.

### Apparatus

Fourier transform infrared (FTIR) spectroscopy analyses were carried out with a Magna-IR 550 spectrometer (KBr pellets; 32 scans/min, resolution 4  $\text{cm}^{-1}$ ).

For proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) a Bruker AC400 was used with tetramethyl silane (TMS) as an internal standard. Analyses were carried out at 110°C using deuterated dimethyl sulfoxide (DMSO) as solvent for P(U-*b*-MMA) block copolymers and a mixture of tetrachloro ethylene (TCE) and deuterated DMSO (TCE/DMSO = 9/10 mass ratio) for P(U-*b*-S) block copolymers. Characteristic resonance peaks appearing at 3.55–3.56 ppm ( $-\text{OCH}_3$ ) (PMMA); 6.4–6.6 and 6.93–7.23 ppm (aromatic ring) (PS); 7.01–7.04 and 7.34–7.36 ppm (aromatic ring), and 3.8–4.1 ppm ( $\text{CH}_2$ ) (PUMAI) were used to determine the block copolymer compositions.

Size exclusion chromatography (SEC) was performed using a Waters chromatograph equipped with a 6000A pump, a U6K injector, and a double detection (UV at  $\lambda = 254$  nm and the differential refractometer R401). THF was used as an eluent, and the separation was carried out with four microstyragel columns ( $10^5$ ,  $10^4$ ,  $10^3$ , and 500 Å). Peak areas were calculated using the differential refractometer detector response. The average molar masses ( $\bar{M}_n$ ,  $\bar{M}_w$ ) of PUs, PUMAI, and of polymers having PS sequences were determined using polystyrene standards. For polymers and block copolymers having PMMA sequences, PMMA standards (from Interchim) were used. SEC analysis using both detection, refractive index (RI), and ultraviolet absorption (UV) gives useful informations about the block copolymers composition. The sample solution (100  $\mu\text{L}$ ) (1% by

**Table II** Synthesis and Characterization of Polyurethane (PU) and Polyurethane Macroazo Initiators (PUMAI)

PU or PUMAI	Feed Composition (mol Ratio)				Average Molar Masses of PU		
	ACP	MDI	PCL 550	PCL 1000	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$I_p = \frac{\bar{M}_n}{\bar{M}_w}$
PU-1	—	1	1	—	10.7	30.0	2.8
PU-2	—	1	—	1	28.0	74.0	2.6
PUMAI-1	1	20	19	—	10.7	29.3	2.7
PUMAI-2	1	20	—	19	27.0	66.0	2.4

weight of the sample in THF) were injected for RI detection. UV response was in some cases saturated. Dilutions of primary solutions (used for RI detection) to 1% by weight in THF were performed, and the obtained diluted solutions were analyzed in UV spectroscopy. All samples provide an UV absorption in agreement with Beer Lambert's law.

Cloud-point measurements or turbidimetric titrations were determined with a light transmission device,<sup>27</sup> a technique that detects particles with average diameters in the order of 0.1  $\mu\text{m}$ . This technique is one of the best for determining the nonsolvent/solvent pair used for each fractionation of the crude block copolymer. Solutions of polymers, polymer blends, and block copolymers in 2-butanone were prepared in glass tubes. The nonsolvent was added gradually. The mixture was shaken by hand, then the measurement of light transmission was performed at room temperature (22°C). A decrease in the transmitted light intensity was recorded for a certain volume ratio : nonsolvent/solvent for each sample.

The glass transition temperature,  $T_g$ , and the change of heat capacity,  $\Delta C_p$  at  $T_g$  were recorded by differential scanning calorimetry (DSC) using a Mettler TA3000 calorimeter. Standard aluminum sample pans were used. Samples (5–10 mg) were weighed directly in the pan, and an empty pan was used as a reference. Both pans were heated at heating rate of 10°C/min under argon. The onset value was taken for  $T_g$  measurements.

#### Preparation of Typical Polyurethane (PU) and Polyurethane Macroazo Initiators (PUMAI)

The polyurethane synthesis based on polyester segments (PU-2, Table II) occurs by the polycondensation of a stoichiometric mixture of MDI (25.5 g) with PCL (102 g) ( $\bar{M}_n = 1000$  g/mol) in 2-butanone at 35°C for 24 h with a catalyst, SnDBDL, [SnD-

BDL]/[NCO] = 0.05% (by mol). The resulting polymer was isolated by drying a thin film layer in vacuum at room temperature for 1 day.

Polyurethane containing azo groups were prepared in a two-stage reaction procedure. The first stage of a typical PUMAI synthesis (PUMAI-2, Table II) is the reaction of ACP (1 g) with a large excess of MDI (25.5 g), i.e., with the molar ratio  $r = [\text{NCO}]/[\text{OH}] = 20$ . The reaction occurs in 2-butanone (260 g) at 25°C for 3 h with SnDBDL as a catalyst [SnDBDL]/[NCO] = 0.05% (by mol). In the second stage, the NCO-terminated radical initiator was chain extended with PCL (96.94 g) ( $\bar{M}_n = 1000$  g/mol). The product was kept in solution at 0–4°C before use for block copolymerization with methyl methacrylate or styrene. Reaction conditions are similar for PU-1 and PU-2 synthesis where the overall stoichiometric ratio ( $[\text{NCO}]/[\text{OH}] = 1$ ) was maintained.

#### Preparation of PMMA and PS Homopolymers; P(U-*b*-MMA) and P(U-*b*-S) Block Copolymers; and PU/PMMA and PU/PS Polymer Blends

With the purpose of comparing poly(urethane-*block*-methylmethacrylate), P(U-*b*-MMA), and poly(urethane-*block*-styrene), P(U-*b*-S) block copolymers with their homologous homopolymers PMMA and PS (alone or blended with polyester-urethane, PU-2) two sets of radical polymerization were carried out in the same conditions but with different initiators. ACP and AIBN were used for the synthesis of PMMA and PS, respectively, whereas PUMAI-2 was used for obtaining the block copolymers. For radical polymerization, typically a mixture of initiator (ACP 0.196 g or PUMAI-2, 24 g) and monomer (MMA, 40 g or S, 41.6 g), which corresponds to a molar ratio  $[\text{N}=\text{N}]/[\text{MMA}] = 1/400$ , in 2-butanone as solvent (80 g) was heated to 80°C under stirring, for 20 h in argon atmo-

**Table III** Different Structural Transformations and Reactions of Various PUMAI s Recorded by DSC Measurements

PU or PUMAI	$T_g^a$ (°C)	$T_g^b$ (°C)	$\Delta C_p^a$ (J/g · K)	$\Delta C_p^b$ (J/g · K)	$T_p^{a,c}$ (°C)	$\Delta H_d^{a,d}$ (kJ/mol)
PU-1	-16.4	-16.0	0.44	0.47	—	—
PU-2	-33.8	-33.5	0.41	0.40	—	—
PUMAI-1	-19.0	-12.5	0.37	0.40	134.0	137.7
PUMAI-2	-31.8	-30.9	0.36	0.38	131.8	128.0

<sup>a</sup> First scan (heating rate 10°C/min from -100 to 180°C) (values  $\pm$  0.5°C).

<sup>b</sup> Second scan after azo decomposition (heating rate 10°C/min -100 to 180°C) (values  $\pm$  0.02).

<sup>c</sup>  $T_p$  temperature at the peak of the exothermic curve for azo and macroazo initiators.

<sup>d</sup>  $H_d$  decomposition enthalpy of azo units (kJ/mol [N=N]) (error 5%).

<sup>e</sup> From ref. 21.

sphere to yield homopolymers or block copolymers. PMMA and PS were purified by precipitation in a large excess of methanol and dried at room temperature for 3 days, then in vacuum at 100°C for 1 h and weighed.

Purification of the block copolymers was more complicated and required the fractionation process described below. So, at first, only the yield of the crude block copolymers obtained was determined by weighing the nonvolatile residue of a thin film layer obtained at 25°C for 3 days, then in vacuum at 60°C for 24 h. Polymer blends of PU/PMMA or PU/PS having the same composition as the block copolymers initiated by PUMAI-2 were prepared by mixing  $v_1$  (mL) of a solution of PU-2 (Table II) in 2-butanone (10% by weight) with  $v_2$  (mL) of a solution of PMMA-1 or PS-1 (Table III) in 2-butanone (10% by weight) to yield the polymer blend with the desired composition. Solvent evaporation occurred at room temperature for 3 days then under vacuum at 60°C for 24 h.

### Fractionation of Block Copolymers

Some conditions have to be fulfilled to obtain an efficient separation by fractionation/precipitation. First, the initial solution of the crude block copolymer should be as diluted as possible. Concentrations of 1% (by weight) are used. Then, the difference between the volume ratio of nonsolvent to solvent for the related homopolymers should be as high as possible. Finally, the volume ratio of nonsolvent to solvent for the first precipitated polymer should be as small as possible to prevent the use of high volumes. According to these considerations cloud-point measurements were used to determine the best choice of pairs nonsolvent/solvent for the crude block copolymers, P(U-*b*-

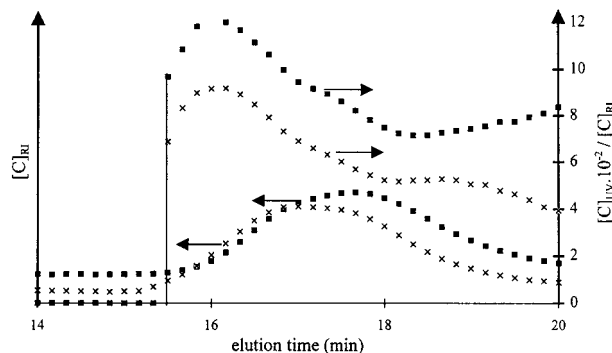
MMA) and P(U-*b*-S). Typically, a quantity *m* g of the crude block copolymer P(U-*b*-MMA) was dissolved in  $v_1$  mL of acetone, then  $v_2$  mL of methanol were slowly added to the vigorously stirred polymer solution at 22°C until the solution became cloudy. The solution was heated to 40°C, then allowed to cool slowly to 22°C. Within 2 to 4 days, the first fraction was precipitated. About 10 fractions were collected using this procedure.

## RESULTS AND DISCUSSION

### PUMAI Synthesis

As explained in the Experimental part, a two-stage reaction procedure was used. In our preceding article<sup>25</sup> we showed that in the first stage of the PUMAI synthesis side reactions may occur by hydrolysis of some isocyanate groups due to moisture yielding the formation of urea. This kind of side reaction should not affect the reactivity of PUMAI s, but is responsible for the formation of lower molar masses that can be seen on SEC curves (RI detector) (Fig. 1). In parallel, Table II shows the feed composition, the number, and mass average molar masses of PUMAI and a comparison with PU that does not contain azo groups. From Table II, it appears that the incorporation of small amounts of azo groups modifies slightly their chain lengths. When the [N=N] concentration increases,  $\bar{M}_n$  and  $\bar{M}_w$  decrease. The rather high value of  $I_p$  is certainly due to some side reactions leading to the formation of urea consuming N=C=O functions and thus modifying the stoichiometry of the mixture.<sup>25</sup>

SEC was also used to detect azo groups. As both aromatic cycles and azo groups in PUMAI s



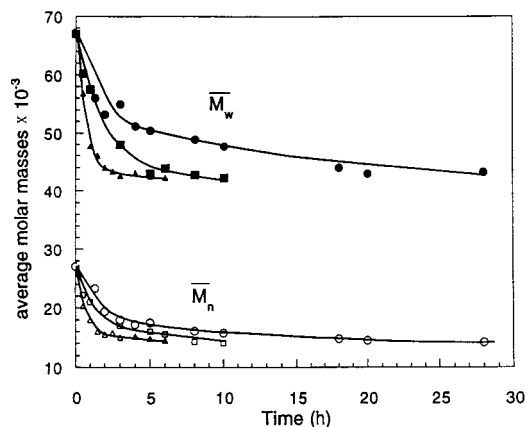
**Figure 1** SEC chromatograms obtained with RI detector and UV/RI ratio for a typical polyurethane and polyurethane macroazo initiator based on polyester segments PU-2, and PUMAI-2: (×) PU-2; (■) PUMAI-2.

absorb at 254 nm, the presence of azo groups in PUMAI (Table II) can be detected using the ultraviolet overrefractive index responses UV/RI in SEC measurements. This ratio UV/RI is compared to that of classical PU (Fig. 1). For example, the ratio UV/RI for PUMAI-2 is between 7 and 12, whereas the same ratio for PU-2 is between 5 and 9. This difference proves the presence of azo units in the PUMAI chains. Moreover, as the difference between the two UV/RI curves of PU-2 and PUMAI-2 vs. elution time remains almost constant, it means that there is the same average value of azo group per chain independent of the chain lengths. As a quantitative analysis is difficult with this method and as it was shown that ACP reacted quantitatively with an excess of MDI<sup>25</sup> in similar conditions as those used in this work, the average content of azo groups in the PUMAI chains can be determined by calculating the ACP content in the feed (Table II).

The solubility tests of PUMAI based on PCL in different solvents were investigated at room temperature. PUMAI are soluble in many solvents such as tetrahydrofuran, acetone, 2-butanone, toluene, 1,4-dioxane, *N,N*-dimethyl formamide, and dimethyl sulfoxide. In the meanwhile, they are not soluble in water, *n*-hexane, methanol, or ethanol.

As polymer azo compounds are to be used as macroazo initiators in radical polymerization and in the synthesis of block copolymers, it is necessary to study the structural transformations when they undergo an increase in temperature. For this purpose, the decomposition enthalpy  $\Delta H_d$ , the temperature at the maximum of exotherm ( $T_p$ ) were recorded by DSC (Table III). Moreover, the glass transition temperature,  $T_g$ ,

and the change of heat capacity,  $\Delta C_p$ , at  $T_g$ , were recorded twice: before and after decomposition for compounds having azo groups. From Table III we can notice that  $T_g$  depends only on the composition (proportions of PCL and MDI, average molecular masses of PCL) of the chain and does not depend on the quantity of azo groups, which is probably too low. A slight increase in  $T_g$  values after PUMAI's decomposition were observed. Each PUMAI showed an exothermic peak due to the decomposition of azo units in polymer chains. The peak of the exothermic curve ( $T_p$ ) of PUMAI were similar to each other and the heat of decomposition of the azo units  $\Delta H_d$  seems to be almost the same.  $\Delta H_d$  is of 120 kJ/mol for ACP and of about 130 kJ/mol for PUMAI-1 and PUMAI-2. SEC chromatograms of PUMAI-2 before and after decomposition with a ramp of temperature under argon shows only a slight evolution toward low molecular masses. This suggests that, in the absence of solvent or vinyl monomers and under argon, there is recombination of the radicals formed after the azo group elimination. The thermal decomposition of PUMAI-2 (1 g) was also investigated in 2-butanone (2 g) and in the presence of a large excess of hydroquinone (HQ) as a radical scavenger, with a molar ratio  $[HQ]/[N=N] = 10$ . The thermal decomposition of azo groups in PUMAI-2 (20 h) in presence of HQ yields polyurethane fragments with  $\bar{M}_n$  and  $\bar{M}_w$  in the range of 13,000 to 14,000, and 43,000 to 44,000 g/mol, respectively. Those values are very superior to the ones of the polycaprolactone used in the PUMAI synthesis, indicating that the decomposition does not affect the ester functions. The number of chain scissions per molecule,  $N_s = \bar{M}_{n(t=0)}/\bar{M}_{n(t=20h)} - 1$ , where  $\bar{M}_{n(t=0)}$  and  $\bar{M}_{n(t=20h)}$  denotes the number average molar mass before ( $t = 0$ ) and after ( $t = 20$  h) thermolysis of  $-N=N-$  units, is found to be about 1. This implies that PUMAI-2 looks like a type I macroazo initiator. The ratio  $\bar{M}_{w(t=0)}/\bar{M}_{w(t=20h)} - 1 = 0.67$  shows that the azo position is not strictly in the middle of polymer chains, which implies that PUMAI-2 chains are statistically disymmetrical to the azo position. Figure 2 shows the evolution of molar masses against time at different temperatures of decomposition, 80, 90, and 100°C. For example, at 80°C after 20 h, almost all azo units were decomposed. Finally, from all the previous analyses, it appears that PUMAI-2 having almost one azo unit per chain and combine rather high  $\bar{M}_n$  and  $\bar{M}_w$  values shows interest and can be chosen for the subsequent radical copolymerization stage.



**Figure 2** Thermal decomposition of PUMAI-2 at different temperatures in 2-butanone in the presence of a large excess of hydroquinone: open symbols  $\bar{M}_n$  values; full symbols  $\bar{M}_w$  values; (●) 80°C; (■) 90°C; (▲) 100°C.

### Radical Polymerization and Characterization of the Crude Block Copolymer

2-Butanone, which presents low transfer reaction in comparison with other experimented solvent, was chosen for the synthesis, as it is also the solvent of PUMAI synthesis and of PMMA and PS. The molar ratio of azo [N=N] groups to [S] or [MMA] used for the synthesis of block copolymers were varied from 1/1000 to 1/150. Table IV gives the results. In all cases, we can notice that the whole consumption of MMA was higher than that of S due to a higher propagation rate. The yield of the crude block copolymers decreased with decreasing azo to monomer ratio. As expected, the number and mass-average molar masses increased with decrease in this ratio as a result of initiating a few polymer chains for the same quantity of the monomer.

For the termination mechanism at 80°C, the MMA polymerization is known to terminate both via disproportionation (80%) and recombination (20%),<sup>28</sup> while styrene polymerization is known to terminate via recombination exclusively.<sup>28</sup> Thus, block copolymerization of MMA should produce mainly AB-type block copolymer, whereas, when the added monomer tends to terminate via recombination (e.g., styrene), the block copolymers are of the ABA-type. The length of PU segments in the block copolymer is determined by the polyester (PCL) average molar masses and the ratio of monomers used for the PUMAI synthesis, whereas the length of PS or PMMA blocks can be controlled by the monomer to macroazo ratio,  $[M]/[-N=N-]^{0.5}$ , the propagation rate, and the

**Table IV** Polymerization of Methyl Methacrylate (MMA) and Styrene (S) Using Azo and Macroazo Initiators

No.	Reaction Products	Monomer [M]	Initiator (I)	Mass (g)	[N=N]/[M]	Solvent Mass (g)	Reaction Time (h)	Yield <sup>a</sup> (%)	PU Content <sup>b</sup> (%)	Polymer $\bar{M}_n \times 10^{-3}$	Polymer $\bar{M}_w \times 10^{-3}$
1	PMMA-1	MMA	AIBN	0.164	1/400	2-butanone 80	6	98	—	41	68
2	PS-1	S	AIBN	0.400	1/400	2-butanone 200	24	48.4	—	16	42
3	P(U- <i>b</i> -MMA)-1	MMA	PUMAI-2	24	1/1000	2-butanone 200	24	80	27.9	94	286
4	P(U- <i>b</i> -MMA)-2	MMA	PUMAI-2	24	1/400	2-butanone 80	24	98	41.4	69	194
5	P(U- <i>b</i> -S)-1	S	PUMAI-2	24	1/1000	2-butanone 210	24	28	51.0	55	131
6	P(U- <i>b</i> -S)-2	S	PUMAI-2	22	1/150	2-butanone 30	24	37	82.7	30	93
7	P(U- <i>b</i> -S)-3	S	PUMAI-2	12	1/1000	Bulk —	24	20	56.2	58	156

<sup>a</sup> Determined by weighing nonvolatile residues after evaporation at room temperature in thin layer film for 3 days.

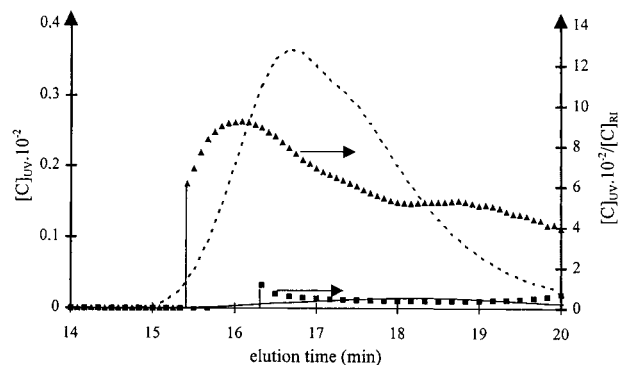
<sup>b</sup> Determined by <sup>1</sup>H-NMR.

<sup>c</sup> Determined from composition on feed.

temperature at which the block copolymerization is carried out.<sup>24</sup>

It is known for radical polymerization that many transfer reactions may occur. To determine the ability of polyurethane chains to behave as transfer agent, the radical polymerization of MMA (50 g) was performed in 2-butanone solvent (80 g) and initiated by AIBN (0.082 g) in the presence of PU-2 (12 g) to yield a PMMA/PU-2 blend. If any transfer reaction on PU-2 chains may occur, it will lead inevitably to P(U-*g*-MMA) copolymer and, therefore, will increase the average molar masses of the mixture. Average molar masses values obtained for PMMA/PU-2 synthesis (MMA polymerized in the presence of PU-2) are slightly higher ( $\bar{M}_n = 5240$ ,  $\bar{M}_w = 1202$ ) than that found for PMMA-3, prepared in the same conditions as previously but without PU-2 ( $\bar{M}_n = 5050$ ,  $\bar{M}_w = 934$ ). We can then conclude that a polyurethane based on MDI and PCL is a very weak transfer agent.

Radical block copolymerization using macroazo initiators leads inevitably to some quantity of the homopolymer, and fine characterization requires fractionation of the reaction mixture. As fractionation is a rather long procedure, the first characterizations were carried out on the crude reaction mixture. Composition and molar masses of crude block copolymers are summarized in Table IV. The crude block copolymer structure was first assigned by means of spectral measurements. The IR spectrum of the block copolymer shows the characteristic bands of both PU and PMMA or PS segments. In the infrared spectra of the reaction products corresponding to references P(U-*b*-MMA)-2, PU-2, and P(U-*b*-S)-2, peaks at 3346 or 3356  $\text{cm}^{-1}$  were observed in all crude block copolymers. This absorption is due to the —NH stretching in the —NH—CO of the polyurethane segments. PMMA segments are assigned by the C—O stretching at 1149.5  $\text{cm}^{-1}$  in the O=C—OCH<sub>3</sub>. And finally, the PS segments are identified by the peaks at 698 and 3026  $\text{cm}^{-1}$  due to the CH vibration in the aromatic cycle. The composition of crude block copolymers P(U-*b*-MMA) was determined from the molar ratio of PU [ $\delta = 7.34\text{--}7.36$  ppm (CH) for two aromatic cycles] to PMMA [ $\delta = 3.55\text{--}3.56$  ppm (O—CH<sub>3</sub>)] in the <sup>1</sup>H-NMR spectra. For crude block copolymers P(U-*b*-S), the composition was determined from the ratio of PU ( $\delta = 7.34\text{--}7.36$  ppm or 3.8–4.1 ppm for CH<sub>2</sub>) to PS (6.93–7.23 ppm, CH of the aromatic cycle). IR and <sup>1</sup>H-NMR analyses do not constitute a proof for block copolymer formation; they give

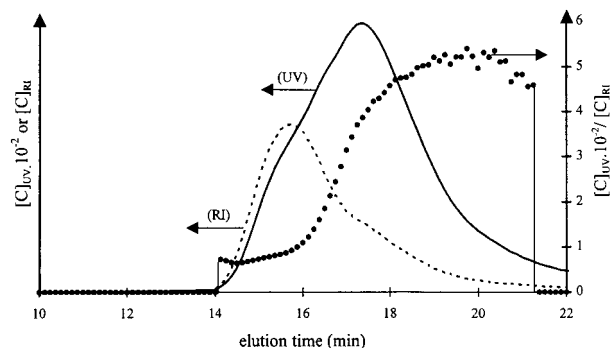


**Figure 3** SEC chromatograms obtained for PS and PU using UV detection at 254 nm and UV/RI. UV: (—) PS; (----) PU; UV/RI: (■) PS, (▲) PU.

only informations on the different sequences and their overall composition in the sample. Nevertheless, from those results, it appears that, in the conditions of this work, the homopolymerization as well as the copolymerization is more difficult with S than with MMA. Indeed, the yield of polymerization,  $\bar{M}_n$  and  $\bar{M}_w$  of PMMA and P(U-*b*-MMA) are always superior to those obtained for PS and P(U-*b*-S) due to propagation rate<sup>29</sup> (Table IV). When bulk polymerization occurs, the yield was slightly lowered (experiment 7 in Table IV), and a slight increase of average molar masses is obtained due to the absence of transfer reaction to the solvent. The % of PU is always bigger in P(U-*b*-S) copolymers and can reach 82.7% (experiment 6 in Table IV).

In contrast to IR and <sup>1</sup>H-NMR, SEC detection by both refractive index and ultraviolet recording allowed a clear assignment of the block copolymer formation. As the homopolymer PMMA is UV transparent, PS has a little absorbance (0.02 in arbitrary unit), and PU has high absorbance (0.37 in arbitrary unit) at 254 nm, of the UV detector (Fig. 3), we can determine the ratio of UV absorption over RI detection to have an idea about the nature of polymers or chains segments at different elution times. This ratio is about 0 for PMMA, 0.4 for PS, and 4 to 8 for PU (without azo groups). Figure 4 shows a typical SEC chromatogram (RI, UV, and UV/RI) of P(U-*b*-MMA)-1. An UV/RI ratio of 0.5 for elution times under 16 min (high molar masses) proves the formation of block copolymer. The abrupt increase of UV/RI ratio after an elution time of 16 min proves the existence of some polymer chains rich in PU or PU homopolymer. The possible formation of PU homopolymer is due to combination of PU radicals formed by





**Figure 4** SEC chromatograms obtained for P(U-*b*-MMA)-1: (----) RI detector; (—) UV detector at 254 nm; (●) UV/RI.

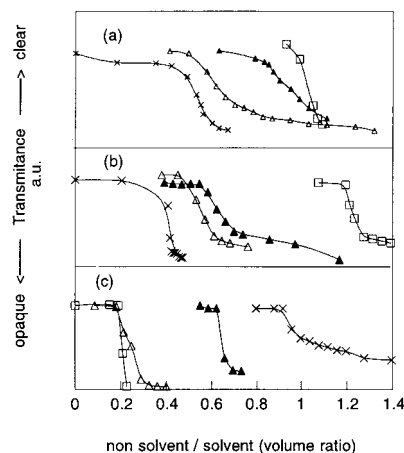
the PUMAI dissociation. The crude block copolymers P(U-*b*-MMA) or P(U-*b*-S) contain a small amount of PU so that the products require careful separation before the block copolymer can be characterized.

#### Fractionation and Characterization of Block Copolymers Fractions

Cloud-point measurements were used to determine the best choice of nonsolvent/solvent for P(U-*b*-MMA)-1, P(U-*b*-S)-1, and P(U-*b*-S)-2. The nonsolvent/solvent pairs available for fractionation of each block copolymer are listed in Table V. Figure 5 shows the cloud-point measurements of P(U-*b*-MMA)-1, P(U-*b*-S)-1, P(U-*b*-S)-2, the corresponding homopolymers, and the polymer blends of the corresponding blocks having the same composition as the block copolymers. Acetone and 2-butanone are used as solvents for P(U-*b*-MMA) and P(U-*b*-S), respectively. Methanol, *n*-hexane, and ethanol are used as nonsolvents for P(U-*b*-MMA)-1, P(U-*b*-S)-1, P(U-*b*-S)-2, respectively.

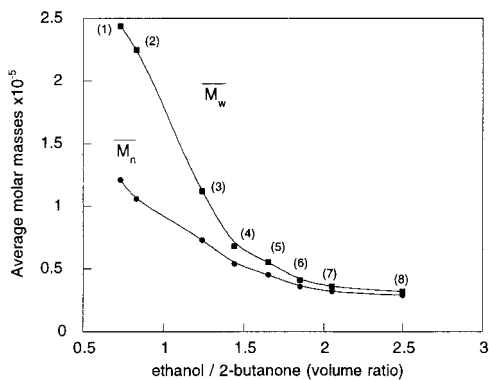
**Table V** Nonsolvent/Solvent Volume Ratio for the First Cloud Appearance for PU, PMMA, and PS Determined by Cloud Point Measurement

Nonsolvent/Solvent	PU	PMMA	PS
Methanol/THF	1.32	1.47	—
Methanol/acetone	0.45	1.00	—
Hexane/cyclohexanone	0.75	—	2.25
2-Propanol/cyclohexanone	1.65	—	0.95
Hexane/2-butanone	0.40	0.60	1.15
2-Propanol/2-butanone	0.95	—	0.25
Methanol/2-butanone	0.70	1.15	0.15
Ethanol/2-butanone	0.90	—	0.20



**Figure 5** Cloud point measurements of block copolymers P(U-*b*-MMA)-1, P(U-*b*-S)-1, and P(U-*b*-S)-2, their relative homopolymer and polymer blends: (a) (×) PU; (Δ) PU/PMMA blend 24 : 76 w/w; (▲) P(U-*b*-MMA)-1; (□) PMMA nonsolvent/solvent : methanol/acetone; (b) (×) PU; (Δ) PU/PS blend 51 : 49 w/w; (▲) P(U-*b*-S)-1; (□) PS nonsolvent/solvent : hexane/2-butanone; and (c) (×) PU; (Δ) PU/PS blend 83 : 17 w/w; (▲) P(U-*b*-S)-2; (□) PS nonsolvent/solvent : ethanol/2-butanone.

The choice of those nonsolvents was made basing on the difference between volume ratio for the first cloud appearance for homopolymers (PU and PMMA or PS) and also crude block copolymers (Fig. 5). As P(U-*b*-S)-1 and P(U-*b*-S)-2 have different composition and masses, the nonsolvents used for their respective fractionation are different. From Figure 5 it appears that the polymers made with PUMAI have not the same solubility as their homologous polymer blends, indicating that they are real copolymers. For a typical example of fractionation experiments, 2.8 g of the crude block copolymer P(U-*b*-MMA)-1 were dissolved in 354 mL of acetone. Then, the first fraction is precipitated with a given volume of nonsolvent, methanol. The yield of fractionation (sum of the separated fraction masses over the starting block copolymer mass) carried out on crude P(U-*b*-MMA)-1 is estimated to 88%, whereas those corresponding to P(U-*b*-S)-1 and P(U-*b*-S)-2 are estimated to 80.5 and 73.75%, respectively. For P(U-*b*-S)-2 block copolymer, Figure 6 shows a decrease of the average molar masses of the different fractions analyzed by SEC with nonsolvent/solvent volume ratio. Thereafter, fractionation occurs not only according to structures but also to molar masses. SEC measurements using the UV/RI ratio and <sup>1</sup>H-NMR (Table VII) show that only the first precipitated fractions 1 and 2 are block co-



**Figure 6** Average molar masses evolution of the fractionated P(U-*b*-S)-2 as a function of ethanol/2-butanone volume ratio: (●)  $\bar{M}_n$ ; (■)  $\bar{M}_w$ .

polymers and the fractions 3 to 8 are essentially PU homopolymers. Such PU chains can be explained by dead fragments and did not act as macroazo initiator during reaction due to diffusion of macro radicals in a viscous solution: the so-called cage effect.<sup>30</sup> So, as it could be expected, too high a concentration of azo groups relative to the styrene monomer concentration results in a nonquantitative yield of block copolymer.

Figures 7 and 8 show the evolution of average molar masses vs. volume ratio nonsolvent/solvent for P(U-*b*-MMA)-1 and P(U-*b*-S)-1 block copolymers. SEC measurements, IR, and <sup>1</sup>H-NMR analyses (Tables VI and VIII) suggest that the first fractions (1 and 2) with the lower molar masses were essentially PU dead fragments. From those figures and for both P(U-*b*-MMA)-1 and P(U-*b*-S)-1 we can notice that fractionation occurs essentially according to the structure from fraction 1 to 4 (PU dead fragment fractions 1 and 2, block copolymers with high PU content for fractions 3 and 4). Then fractionation occurs essentially according to molar masses (Tables VI and VIII). The fractionation experiments and the urethane titrations in the fractions (Tables VI–VIII) clearly show that the polymerization syntheses lead to the formation of real copolymers with more or less polyurethane homopolymer. The concentration of this homopolymer depends on the reaction conditions and on the  $[N=N]/[M]$  ratio. When its concentration is rather low, it is probably not indispensable to extract it from the reaction medium for a subsequent use of the copolymer. But, if necessary, the homopolymer can be removed by fractionations using appropriate nonsolvent/solvent couples. SEC chromatograms of fractions of P(U-*b*-MMA)-1 are shown in Figure 9. We can

**Table VI** Average Molar Masses and Composition of the Fractions Obtained from 4 g of the Crude Block Copolymer P(U-*b*-S)-1 ( $\bar{M}_n = 55,000$ ,  $\bar{M}_w = 131,000$ , %PU = 51)

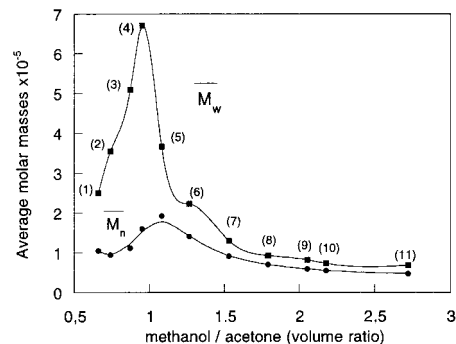
Fraction	Nonsolvent/Solvent Volume Ratio Hexane/2-Butanone	Mass of Samples m (g)	Percentage of Homo- polymers and of Triblock Copolymers		Molar Masses (SEC) (Polystyrene Standards)						Percentage of PU (=A) in the Sample Corresponding to			
			ABA (%)	A (%)	Overall		ABA		A		A + ABA (Overall) (NMR)	Triblock Copolymers		Homopolymer A [eq. (2)]
					$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$		ABA [eq. (3)]	Homopolymer A [eq. (2)]	
1	0.609	0.09	—	100.0	73	125	—	—	73	125	90.0	UD	90.0	
2	0.914	0.29	—	100.0	46	85	—	—	46	85	94.2	UD	94.2	
3	1.170	0.82	85.6	14.4	67	158	157	218	32	41	61.0	46.6	52.5	
4	1.32	0.96	91.2	8.8	67	229	132	268	18	21	61.3	52.5	14.4	
5	1.520	0.16	93.8	6.2	74	181	110	192	12	14	24.8	18.6	8.8	
6	1.726	0.31	96.3	3.7	83	182	111	189	11	13	21.3	17.6	6.2	
7	1.929	0.20	96.7	3.3	70	118	88	122	10	11	18.2	14.9	3.7	
8	2.136	0.12	94.0	6.0	55	94	75	98	9	10	20.7	14.7	3.3	
9	2.643	0.15	97.0	3.0	40	86	63	90	6	8	17.0	14.5	6.0	
10	3.455	0.12	93.3	6.7	30	52	55	44	5	6	16.1	14.1	2.5	

UD, undetected.

**Table VII** Average Molar Masses and Composition of the Fractions Obtained from 4 g of the Crude Block Copolymer P(U-*b*-S)-2 ( $\bar{M}_n = 30,000$ ,  $\bar{M}_w = 93,000$ , %PU = 82.7)

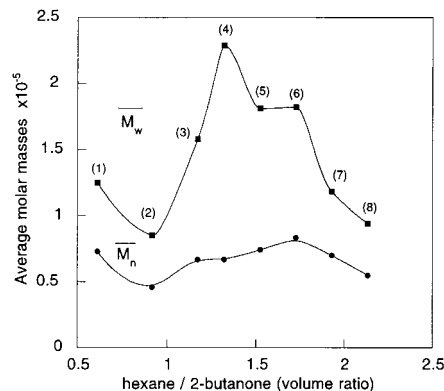
Fraction	Nonsolvent/ Solvent Volume Ratio	Mass of Samples m (g)	Percentage of Homopolymers and of Di- + Triblock Copolymers		Molar Masses (SEC) (Polystyrene Standards)						Percentage of PU (=A) in the Sample Corresponding to		
			ABA (%)	A (%)	Overall		ABA		A		A + ABA (Overall) (NMR)	Triblock Copolymers ABA [eq. (3)]	Homopolymer A [eq. (2)]
					$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$			
1	0.73	0.39	≈ 100	UD	121	244	121	244	—	—	26.4	26.4	UD
2	0.83	0.28	≈ 100	UD	106	225	106	225	—	—	32.2	32.2	UD
3	1.24	0.92	UD	≈ 72	73	112	—	—	73	8.0	80.1	8.0	72.0
4	1.44	0.40	UD	≈ 94	54	68	—	—	54	2.1	94.1	2.1	92.0
5	1.65	0.23	UD	≈ 96	45	55	—	—	45	2.5	96.5	2.5	94.0
6	1.85	0.32	UD	≈ 96	36	41	—	—	36	1	97.0	1	96.0
7	2.05	0.11	UD	≈ 96	32	36	—	—	32	1	96.8	1	96.8
8	2.50	0.15	UD	≈ 96	29	32	—	—	29	1	96.7	1	96.7
9	3.10	0.15	UD	≈ 96	28	30	—	—	28	1	96.5	1	96.5

UD, undetected.



**Figure 7** Average molar masses evolution of the fractionated P(U-*b*-MMA)-1 as a function of methanol/acetone volume ratio: (●)  $\bar{M}_n$ ; (■)  $\bar{M}_w$ .

notice from Figure 9(a) that fractions 2 to 4 are bi- and trimodal chromatograms assigned by A, AB, and ABA. According to molar masses and to UV/RI ratio (fraction 4, Fig. 10), higher molar masses are attributed to di-AB and tri-ABA block copolymers, while A corresponds to polyurethane homopolymer. From fraction 5, SEC chromatograms are bimodal and contain essentially diblock (AB) copolymers, and polyurethane homopolymer (A) according to molar masses and the UV/RI ratio. The last fractions obtained are essentially block copolymers, indicating that any PMMA homopolymer was formed during the radical polymerization. For P(U-*b*-S)-1, fractions 3 to 8 are bimodal and are noticed by ABA and A. Higher molar masses are attributed to triblock ABA copolymers, as termination of polystyrene radical chain polymerization is known to occur only via recombination mechanism, while A corresponds to a small amount of polyurethane ho-

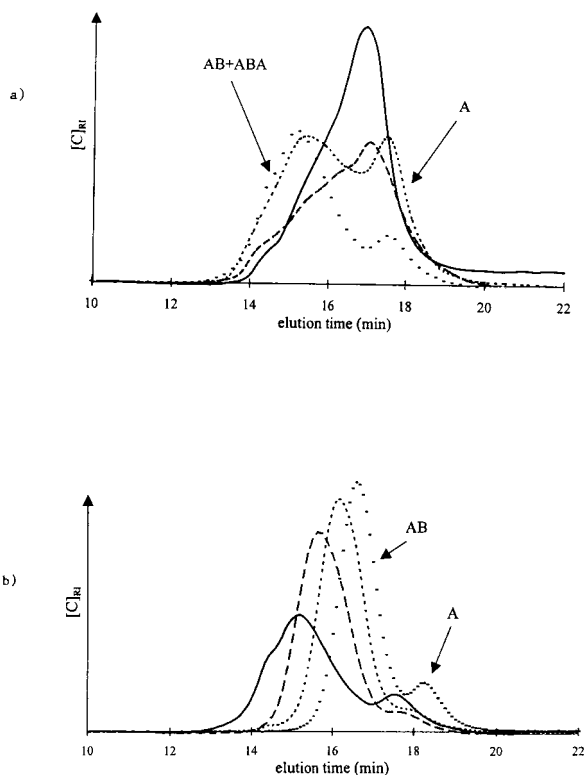


**Figure 8** Average molar masses evolution of the fractionated P(U-*b*-S)-1 as a function of hexane/2-butanone volume ratio: (●)  $\bar{M}_n$ ; (■)  $\bar{M}_w$ .

**Table VIII** Average Molar Masses and Composition of the Fractions Obtained from 2.8 g of the Crude Block Copolymer P(U-*b*-MMA)-1 ( $\bar{M}_n = 94,000$ ,  $\bar{M}_w = 286,000$ , %PU = 27.9)

Fraction	Nonsolvent/ Solvent Volume Ratio Methanol/ Acetone	Mass of Samples m (g)	Percentage of Homopolymers and of Di- + Triblock Copolymers				Molar Masses (SEC) <sup>a</sup>						Percentage of PU (=A) in the Sample Corresponding to						
			AB + ABA (%)		A (%)		Overall			AB + ABA			A			A + AB + ABA (Overall) (NMR)		Di + Triblock Copolymers AB + ABA [eq. (3)]	Homopolymer A [eq. (2)]
			$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$			
1	0.66	0.055	27.5	72.5	105	250	294	474	61.0	79.0	95.4	35.4	35.4	60.0					
2	0.74	0.070	54.5	45.5	94	355	300	685	35.0	56.0	75.7	35.7	35.7	40.0					
3	0.87	0.170	64.1	35.9	111	509	310	760	43.0	55.0	63.0	30.0	30.0	33.0					
4	0.95	0.170	95.2	4.8	160	671	363	912	41.0	48.0	30.2	27.2	27.2	3.0					
5	1.08	0.700	99.1	0.9	192	367	260	398	37.0	42.0	15.0	14.3	14.3	0.7					
6	1.27	0.700	99.2	0.8	140	223	162	231	32.0	35.0	13.8	13.1	13.1	0.7					
7	1.53	0.360	95.8	4.2	91	130	118	145	28.5	30.5	19.2	16.2	16.2	0.7					
8	1.79	0.135	99.1	0.9	70	93	83	105	24.0	27.0	10.5	9.7	9.7	3.0					
9	2.06	0.022	70.5	1.3	59	82	70	95	19.7	20.4	35.6	18.5	18.5	0.8					
10	2.18	0.075	99.2	0.8	55	73	64	82	19.8	21.2	18.9	18.2	18.2	17.1					
11	2.72	0.050	95.6	4.1	47	68	58	74	19.8	21.0	28.3	24.5	24.5	0.7					

<sup>a</sup> Average molar masses of peaks related to polyurethane homopolymers (A) are determined using polystyrene standards, and those related to di- and triblock copolymers P(U-*b*-MMA) (AB and/or ABA) are determined using PMMA standards.

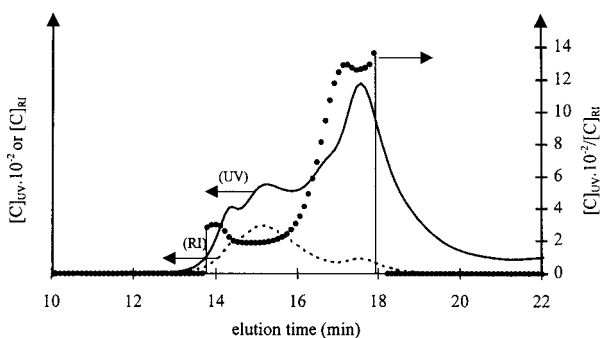


**Figure 9** SEC chromatograms obtained for fractions of P(U-*b*-MMA)-1 (RI detector): (a) (—) fraction 1; (---) fraction 2; (---) fraction 3; (-) fraction 4; (b) (—) fraction 5; (---) fraction 6; (---) fraction 7; (-) fraction 8.

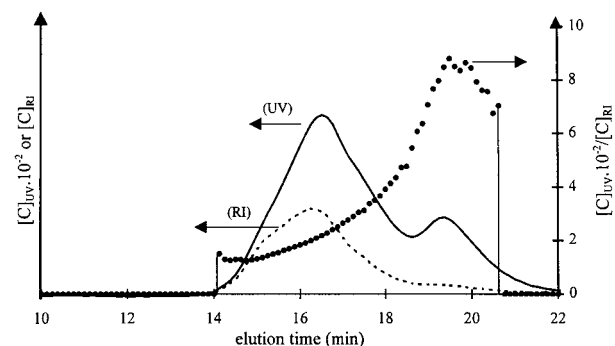
mopolymer of lower molar masses according to UV/RI  $\cong$  8 ratio (fraction 5, Fig. 11).

SEC measurements corroborated with  $^1\text{H-NMR}$  were also used to determine the relative proportions of the individual blocks and homopolymers.

From SEC chromatograms we can determine the percentage of each zone AB and ABA for P(U-



**Figure 10** SEC chromatograms obtained for fraction 4 of P(U-*b*-MMA)-1: (----) RI detector (—) UV detector at 254 nm; (○) UV/RI.



**Figure 11** SEC chromatograms obtained for fraction 5 of P(U-*b*-S)-1: (----) RI detector; (—) UV detector at 254 nm; (○) UV/RI.

*b*-MMA), ABA for P(U-*b*-S) and A (PU) in each chromatogram.

For a fraction (i) the percentage of each zone is determined by measuring the peak area using RI detection from eq. (1).

$$\% \text{ zone (A or AB and/or ABA)} = \frac{\text{area of zone (A or AB and/or ABA)}}{\text{total area}} \times 100 \quad (1)$$

The percentage of polyurethane homopolymer in each fraction can be determined using SEC analysis with RI detection according to eq. (1), therefore neglecting the effect of the difference of the refractive index between PU and PS or PMMA. It can also be found according to eq. (2), for which PUMAI is injected separately and used as internal standard, the amount of polyurethane homopolymer ( $x_A$ ) is then determined with more accurate values.

$$x_A = \frac{[\text{area of zone A}]}{[\text{area of PUMAI}]} \times 100 \quad (2)$$

where  $x_A$  is the amount of polyurethane homopolymer in a given fraction, the area of zone A is the area of the zone (A) corresponding to the polyurethane homopolymer in this fraction, and the area of PUMAI is the surface corresponding to the PUMAI that is used as internal standard in those experiments. The amount of polyurethane blocks ( $x_b$ ) in pure block copolymers (zone AB and/or ABA in SEC chromatograms) in each fraction can be obtained from eq. (3).

$$x_b = x_t - x_A \quad (3)$$

**Table IX** Yield of Fractionation, Percentage of Homopolymer PU, Yield in Block Copolymer of the Crude Block Copolymers P(U-*b*-MMA)-1, P(U-*b*-S)-1, P(U-*b*-S)-2, and Block Efficiency, *be* [eq. (5)] of PUMAI-2

Block Copolymer	Yield of Fractionation	<i>b</i> %	<i>be</i>	% PU Homopolymer
P(U- <i>b</i> -MMA)-1	83.70	92.8	0.56	6.0
P(U- <i>b</i> -S)-1	80.50	80.4	0.52	18.6
P(U- <i>b</i> -S)-2	73.75	22.7	0.09	66.2

where  $x_f$  is the total composition on polyurethane segments in a given fraction determined by  $^1\text{H-NMR}$ .

Finally, yields in block copolymers (*b*%) for the crude block copolymers P(U-*b*-MMA)-1, P(U-*b*-S)-1 and P(U-*b*-S)-2 can be determined from eq. (4) and are listed in Table IX.

$$b(\%) = \frac{\sum_l^n m_i x [\% \text{ zone(AB and/or ABA)}_i]}{\sum_l^n m_i} \quad (4)$$

where  $n$  is the number of fractions,  $m_i$  the mass of a fraction  $i$ ,  $\% \text{ zone (AB and/or ABA)}_i$  the percentage in block copolymer (diblock and triblock or only triblock) of the fraction  $i$ . From Table IX, it appears that if the  $[\text{N}=\text{N}]/[\text{Monomer}]$  ratio is elevated (1/150), it results in a poor block copolymer yield (22.7% for P(U-*b*-S)-2). For  $[\text{N}=\text{N}]/[\text{Monomer}]$  ratios of 1/1000, yields in P(U-*b*-S)-1 and P(U-*b*-MMA)-1 block copolymers are of 80.4 and 92.8%, respectively. It means that for high ratio values of  $[\text{N}=\text{N}]/[\text{Monomer}]$  PU radicals recombinations are exhibited and the percentages of homopolymers PU increase (Table IX). The block efficiency (*be*) of a macroinitiator, as defined by Munmaya,<sup>24</sup> is a ratio of polymer mass connected as a component of block copolymers over the mass of all polymers formed. The block efficiency can be calculated using eq. (5).

$$be = \frac{\sum_l^n m_i x_{b(i)}}{m x_t} \quad (5)$$

where  $x_{b(i)}$  is the polyurethane segment content in the block copolymer for the fraction  $i$ , and  $x_t$

the total polyurethane content in the sample. From Table IX, we can notice that in the case of P(U-*b*-S)-1 and P(U-*b*-S)-2 the yield in block copolymer, (*b*%) and the block efficiency (*be*) of the macroazo initiator decreases with decreasing vinyl monomer concentration. This can be explained by radical pairs formed after the scission of the macroazo initiator that tend to recombine due to slow diffusion rate. Munmaya<sup>24</sup> showed that in the case of insufficient feed of monomer styrene (S), block efficiency became low. Therefore, increasing the block efficiency is reflected by the trend of an increase of the block length (increase of molar masses (Table IV)) with a decreasing of  $[\text{PUMAI}]/[\text{Monomer}]$  or  $[\text{N}=\text{N}]/[\text{Monomer}]$  mol ratio on feed. Kinoshita et al.<sup>15</sup> have found that the block efficiency values of a PUMAI based on dipropylene glycol (DPG), hexamethylene diisocyanate (HMDI), and ACP used for radical polymerization of butyl methacrylate (BMA) were in the range of 0.4–0.5%. From Table IX we can notice also that the block efficiencies of PUMAI-2 for the radical polymerization of S or MMA for  $[\text{N}=\text{N}]/[\text{Monomer}]$  mol ratio equal to  $10^{-3}$  are in the same range [0.56 for P(U-*b*-MMA)-1 and 0.52 for P(U-*b*-S)-1].

## CONCLUSION

Different polyurethane macroazo initiators (PUMAI) with ester functions and with one azo group per chain were synthesized and characterized. A PUMAI was used to initiate radical block copolymerization of methyl methacrylate (MMA) and styrene (S). In both cases, with micro (ACP) or macro (PUMAI) azo initiators the yield of radical polymerization of MMA was higher than with S. Moreover, it was shown that the increasing amount of azo groups provides a decrease in average molar masses. This method of block copoly-

mer synthesis using macroazo initiators leads to a certain amount of polyurethane homopolymer. The fractionation method was established by a choice of a nonsolvent/solvent pair for each kind of block copolymer. SEC analyses corroborated with  $^1\text{H-NMR}$  spectra of the fractions were used to determine the amount of polyurethane homopolymers and of polyurethane segment in the block copolymer that are both increased by the azo vs. monomer ratio. Nevertheless, whereas fractionation is inevitable for a fine analysis of the block copolymers obtained, it is expected that it is not always a necessary step for their subsequent uses. This point will be studied in a following article that focuses on the morphology and mechanical properties of the copolymers obtained in this first set of experiments.

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