Synthesis and Characterization of Block Copolymers Using Polysiloxane Based Macroazoinitiator

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Poly(dimethylsiloxane-b-styrene) (PDMS-*b*-PSt) and poly(dimethylsiloxane-b-methyl methacrylate) (PDMS-*b*-PMMA) block copolymers containing siloxane segments were studied by the radical polymerizations of vinyl monomers such as styrene (St) and methyl methacrylate (MMA) using polydimethylsiloxane based macroazoinitiator (PDM-MAI) in solution. PDM-MAI was synthesized by reacting hydroxy-terminated polydimethylsiloxane (PDMS) and 4,4′-azobis(4-cyanopentanoyl chloride) (ACPC) having a thermodegradable azo-linkage. The polycondensation reaction between PDMS and ACPC (2:1, molar ratio) was carried out at room temperature. The polymerizations of St and MMA initiated by PDM-MAI were investigated using different PDM-MAI concentrations (1, 5, 10, and 15 wt.%) for various reaction times with a methyl ethyl ketone (MEK) / dichloromethane (DCM) solvent mixture (3:1, molar ratio) as the reaction medium at 65 °C. The decomposition temperature of MAI azo groups was determined to be 125 °C by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). PDM-MAI was characterized from the ^{1}H-NMR spectrum, where the signals of the -CH$_2$ resonance (2.32–2.71 ppm) and -CH$_3$ resonance (1.65–1.70 ppm) of ACPC and the dimethylsiloxane protons (0.072 ppm) in siloxane segments are observed. PDM-MAI was also identified by the peak at 1740 cm^{-1} due to the C=O stretching, proving polyester formation, the peaks at 800 and 1260 cm^{-1} as the Si-CH$_3$ deformation bands, and the Si-O-Si asymmetric stretching vibration bands appearing at 1100 cm^{-1} from the FTIR spectrum. The number-average molecular weight ($\bar{M}_n$) of PDM-MAI was determined to be 812 g/mol by vapor pressure osmometry (VPO) in chloroform. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of PDMS-*b*-PSt and PDMS-*b*-PMMA copolymers determined by gel permeation chromatography (GPC) show a decrease with respect to increasing PDM-MAI initial concentration in the polymerization mixture. In addition, the polymerization yields increase with increasing reaction time for constant PDM-MAI concentrations.

Key Words: Polydimethylsiloxane based macroazoinitiator, poly(dimethylsiloxane-*b*-styrene), poly (dimethylsiloxane-*b*-methyl methacrylate), macroazoinitiator, solution polymerization.

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Introduction

The use of polymeric initiators such as a macroazoinitiator (MAI) having labile azo groups is a well-known method for preparing various block copolymers by conventional radical polymerization[1−8]. Synthesis using MAIs provides some advantages. Not only are block copolymers composed of addition polymer segments but also those of addition polymers and various oligomer segments can be synthesized by using MAIs in radical processes. In addition, MAIs enable researchers to combine different kinds of polymerization reactions, where MAIs can be prepared by the use of materials having both polycondensation[9] or polyaddition functionality[10,11]and a thermally labile azo-linkage as radical initiation species[12]. However, it is an important factor to synthesize a MAI containing one or more azo groups in the main chain for the molecular structure of block copolymers. Depending on the type of MAI and termination reaction, diblock (AB), triblock (ABA) or multiblock (AB)$_n$ copolymers can be obtained. Many studies have focused on the preparation of different block copolymers using different types of MAIs by heating in the presence of a vinyl monomer[13,14].

Incorporation of polysiloxane segments into common vinyl polymers would lead to an interesting group of thermoplastic elastomers with low glass transition temperature, high lubricity, high gas permeability, etc. In recent years, many studies were reported with MAIs containing polysiloxane segments for the synthesis of siloxane-vinyl block copolymers[15−23]. The macroazoinitiator prepared by the condensation of 4,4′-azobis(4-cyanopentanoyl chloride) (ACPC) and α,ω-bis(3-aminopropyldimethyl) polysiloxanes in equimolar amounts was found to be a useful candidate for the radical polymerization of vinyl monomers with a typical product of poly(dimethylsiloxane-*b*-methyl methacrylate) (PDMS-*b*-PMMA)[15]. Inoue et al.[15] showed that incorporation of the PDMS segment in block copolymers improved the thermal stability of PSt. Hamurcu et al.[17] reported the production of the block and graft copolymers as PDMS-*b*-Polystyrene (PDMS-*b*-PSt) and PDMS-*g*-Polybutadiene (PDMS-*g*-PBd) by using NH$_2$-terminated PDMS based macroazoinitiators obtained by the reaction of ACPC with α,ω-amine terminated PDMS prepolymer. It was also reported that crosslinked block copolymers of styrene containing poly(dimethylsiloxane) units could be prepared with macroinimer having PDMS units and the thermal properties of crosslinked PDMS-*b*−PSt copolymers were compared with the copolymers of styrene prepared by PDMS-macroazoinitiators[18].

Chang et al.[19]studied the synthesis and thermodecomposition kinetics of hydroxybutyl-terminated macroazoinitiators (PDMS-ACP) of varying molecular weights, and prepared PDMS-*b*-PMMA copolymers using PDMS-ACP macroazoinitiators. It was found that the activation energy (E$_o$), activation enthalpy (ΔH*) and activation entropy (ΔS*) of the thermodecomposition of PDMS-ACP in toluene increased with increases in poly(dimethylsiloxane) chain length (SCL) in PDMS moieties, while the activation free energy (ΔG*) was independent of the SCL. In another study, Chang et al.[20]prepared PDMS-*b*-PSt copolymers with PDMS-ACP macroazoinitiators, investigated the thermal and thermo-oxidative degradation of these copolymers, and found that the incorporation of PDMS segments in the block copolymers improved the thermo-oxidative stability of PSt.

The aim of this study was the synthesis of block copolymers based on polydimethylsiloxane and polystyrene or poly(methyl methacrylate) sequences using different concentrations of PDM-MAI with a MEK/DCM solvent mixture (3:1 molar ratio) as the reaction medium. The indicated MEK/DCM solvent mixture was used to dissolve PDM-MAI completely so that a homogeneous reaction medium was obtained. First, the synthesis of PDM-MAI based on ACPC and hydroxy-terminated PDMS ($\bar{M}_n$ = 500 g/mol)

was performed in one stage. Then various initial amounts of PDM-MAI were used to initiate the radical polymerizations of methyl methacrylate (MMA) and styrene (St) in solution. The main contribution of this study is the use of OH-terminated PDMS as opposed to the NH_2-terminated PDMS used in the literature[17,18]. The characterizations of PDM-MAI and block copolymers synthesized are discussed in detail.
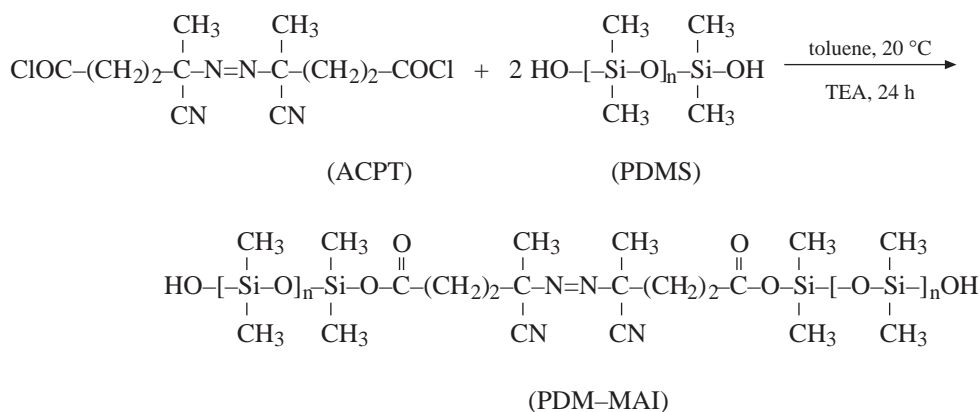
Experimental

Materials

4,4′-Azobis(4-cyanopentanoic acid) (ACPA) was used as received from Fluka AG with better than 98% purity. ACPA was converted to the acid chloride derivative 4,4′-azobis(4-cyanopentanoyl chloride) (ACPC) having a melting point of 97 °C[24]. Hydroxy-terminated polydimethylsiloxane was supplied by Aldrich, and used without further purification. Its molecular weight and hydroxyl functionality were 500 g/mol and 2.0, respectively. St and MMA were purchased from Acros. Monomers were freed of inhibitor by washing in a 5% aqueous NaOH solution and distilled water, and drying over anhydrous Na_2SO_4. Methanol (LabScan), toluene (LabScan), hexane (LabScan), methyl ethyl ketone (MEK) (LabScan), triethylamine (TEA) (JT Baker) and dichloromethane (DCM) (LabScan) were used as dried and purified in the conventional manner.

Preparation of polydimethylsiloxane based macroazoinitiator (PDM-MAI)

The low temperature solution polycondensation method was applied for the synthesis of polydimethylsiloxane based macroazoinitiator having a scissile azo group in the main chain. The reaction for the synthesis of PDM-MAI is shown in Scheme 1. PDM-MAI is prepared as follows: 7.93 g (16 mmol) of OH-terminated PDMS, 3.44 mL of triethylamine (TEA) and 30 mL of toluene were placed into a 250 mL 3-necked and round-bottomed flask equipped with a magnetic stirrer, a thermometer, a dropping funnel, and a reflux condenser having a $CaCl_2$ drying tube. After the flask was cooled in an ice-bath at 0-5 °C, 2.63 g (8.3 mmol) of ACPC in 30 mL of toluene was added dropwise through the dropping funnel over 30 min under stirring. The reaction was continued at room temperature (ca. 20 °C) under stirring for 24 h in nitrogen atmosphere. The reaction mixture's viscosity gradually increased during polycondensation. At the end of the reaction, the resulting viscous mixture was transferred to a separatory funnel, and then it was put into hexane to remove

(ACPT)   (PDMS)

(PDM–MAI)

Scheme 1.

toluene. After filtration, 300 mL of water was added to remove the salt and other soluble components from the product. The washing was repeated to secure the removal of salts and ACPA. The pale yellow waxy solid product was dried under vacuum at room temperature for 3 days, and stored in a refrigerator until use.

Polymerization of vinyl monomers (styrene, methyl methacrylate) using PDM-MAI

The radical solution polymerizations were carried out under the same conditions but with different initial concentrations of PDM-MAI and reaction times to compare the yields and molecular weights of PDMS-*b*-PSt and PDMS-*b*-PMMA block copolymers. The reaction for the synthesis of PDMS-*b*-PSt and PDMS-*b*-PMMA block copolymers is shown in Scheme 2. Polymerizations were carried out in MEK/DCM (3:1, molar ratio) solvent mixture placed in a glass Pyrex tube to dissolve PDM-MAI completely. The total initial content of MAI and monomer (concentration details are given in Tables 1 and 2) in the reaction mixture was 20 wt. %. The reacting components were degassed by 3-fold freeze-thawing cycles. Then the tube containing the monomer, PDM-MAI and the required amount of solvent mixture was immersed in a constant heating bath at 65 ± 1 °C for different reaction times. For each reaction time, the tube contents were evaporated, and then the copolymers were separated by precipitation in methanol, followed by dissolution in CH_2Cl_2, and reprecipitation in methanol. The copolymers obtained were finally dried under vacuum at room temperature to constant weight. The characteristic data and reaction conditions are presented in Table 1 and 2 together with the polymerization results.

Scheme 2.

Characterization of block copolymers

Fourier transform infrared (FTIR) spectroscopy analyses of the macroazoinitiator and block copolymers were performed by a Unicam Mattson 1000 spectrometer (KBr pellets; 100 scans/min, resolution 4 cm^{-1}). A Bruker AC250 was used for the proton nuclear magnetic resonance (^{1}H-NMR) analysis with tetramethylsilane (TMS) as the internal standard. The analysis of macroazoinitiator and block copolymers was performed at room temperature using CDCl$_3$ as the solvent. The number-average molecular weight of MAI was determined with a Knauer type vapor pressure osmometer (VPO) at 30 °C in chloroform. The calibration was carried out with a benzil standard with $\bar{M}_n$ of 210.12. DSC thermograms of block copolymers were also taken on

a Perkin Elmer/Pyris-1 Model apparatus at a heating rate of 5 °C/min under nitrogen atmosphere in the temperature range 100-650 °C. Thermogravimetric analysis (TGA) of macroazoinitiator and copolymers was carried out using a Setaram Labsys TG-DTA12 under nitrogen atmosphere at a heating rate of 10 °C/min. The molecular weights of the block copolymers and their distributions were determined by gel permeation chromatography (GPC) using a Waters chromatograph equipped with an Agilent 1100 RI detector and a Waters HR 5E, 4E, 3, 2 narrowbore column set. Tetrahydrofuran (THF) was used as an eluent, and the elution rate was 0.3 mL/min.

Results and Discussion

PDM-MAI synthesis

MAI containing siloxane units, PDM-MAI, was readily synthesized by the polycondensation of OH-terminated PDMS and ACPC of 2:1 molar ratio feed. The number-average molecular weight ($\bar{M}_n$) of PDM-MAI was found to be 812 g/mol using a vapor pressure osmometer (VPO). The measured $\bar{M}_n$ of PDM-MAI was lower than the stoichiometrically calculated value ($\bar{M}_n = 1246$ g/mol). This may be due to the binding of the OH-terminated PDMS unit largely to 1 instead of the 2 sides of ACPC during the synthesis of PDM-MAI. The exothermic peak and the first-stage weight-loss of PDM-MAI in the TGA thermogram show the exothermic decomposition of the azo group of PDM-MAI at around 125 °C (Figure 1).
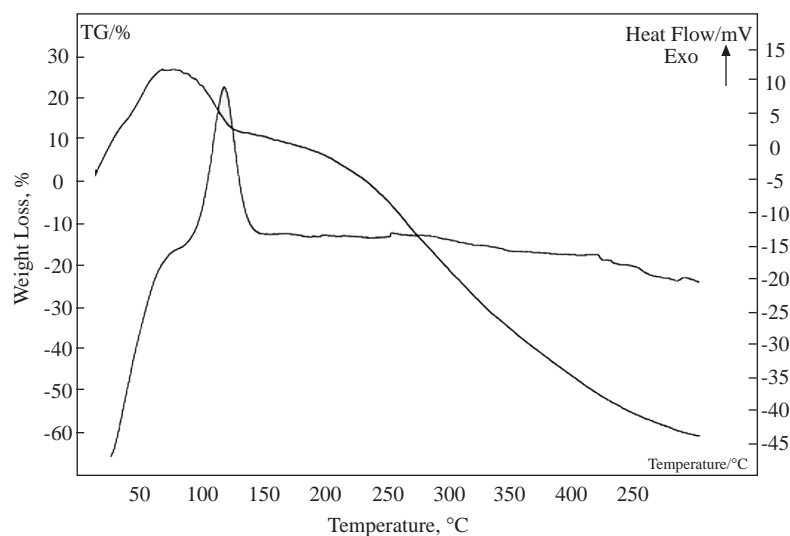
Figure 1. TGA curve of PDM-MAI.

Thermal fragmentation of the PDM-MAI synthesized was performed using TGA in nitrogen atmosphere. Decomposition of the azo groups started at ca. 98 °C, and ended at ca. 125 °C. Further chain scission was found to occur at ca. 200 °C. The percentage weight loss reached at the end of the first derivative peak was 10.6%. The TGA curve of PDM-MAI is shown in Figure 1.

Figure 2 shows the ^{1}H-NMR spectrum of PDM-MAI, where the signals of the -CH$_2$ resonance (2.32–2.71 ppm) and -CH$_3$ resonance (1.65–1.70 ppm) of ACPC and the dimethylsiloxane protons (0.072 ppm) in siloxane segments are observed. The expected structure of the PDM-MAI is confirmed by ^{1}H-NMR spectroscopy, and agrees well with the literature structures of similar compounds[15,17−19].
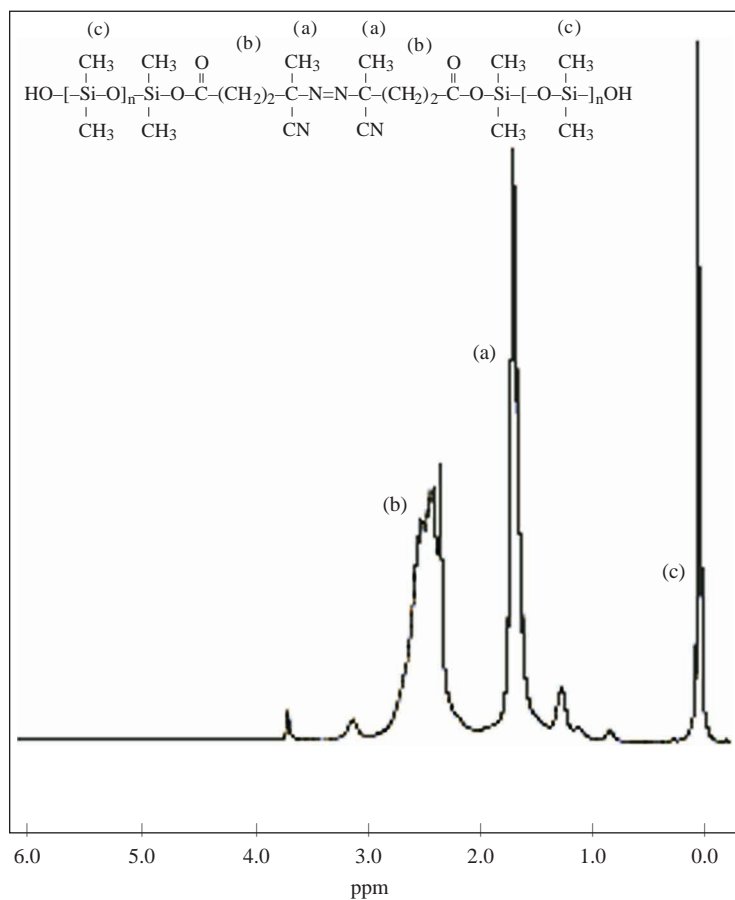
Figure 2. ^{1}H-NMR spectrum of PDM-MAI.

The IR spectrum of PDM-MAI shows the characteristic bands of PDMS segments (Figure 3). PDM-MAI is identified by the peak at 1740 cm^{-1} due to the C=O stretching, proving polyester formation. The characteristic peaks of PDM-MAI were observed at 800 and 1260 cm^{-1} as the Si-CH$_3$ deformation bands, and Si-O-Si asymmetric stretching vibration bands appearing at 1100 cm^{-1} were found[2].

Application of PDM-MAI to synthesis of block copolymers with vinyl monomers

Block copolymerizations of vinyl monomers (St and MMA) were carried out using PDM-MAI at 65 °C. In the polymerization reactions, the initial percentages of macroazoinitiator to monomer for the synthesis of PDMS-*b*-PSt and PDMS-*b*-PMMA block copolymers were varied as 1, 5, 10, and 15 wt. % using different reaction times. The preparation conditions and yields of the resulting block copolymers are given in Tables 1 and 2. The block copolymer yields obtained were estimated gravimetrically.

The IR spectra of the PDMS-*b*-PSt and PDMS-*b*-PMMA show that the characteristic bands of the PDMS segment are observed in all block copolymers obtained at 800, 1260 and 1100 cm^{-1} (Figure 3). These first 2 peaks are due to Si-CH$_3$ deformation, and the third peak is due to Si-O-Si asymetric stretching vibration in the dimethylsiloxane segment. PMMA segments are identified by the C-O stretching at 1719 cm^{-1} in the O=C-OCH$_3$. The PSt segments are determined by the peaks at 700, 1602 and 3026 cm^{-1} due to the CH vibration in the aromatic cycle.

Table 1. Block copolymerization of styrene with PDM-MAI.

Run No.	PDM-MAI (g)	PDM-MAI (wt.% to St)	Reaction Time (h)	Yield (wt.%)	$\bar{M}_n \times 10^3$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	0.009	1	24	17.80	29	1.5
2	0.045	5	24	32.03	13	1.6
3	0.090	10	24	45.10	9	1.5
4	0.135	15	24	58.07	7.5	1.4
5	0.009	1	48	24.97	32	1.7
6	0.045	5	48	41.90	14	1.7
7	0.090	10	48	49.60	9	1.6
8	0.135	15	48	59.03	8	1.5
9	0.009	1	72	25.43	32	1.8
10	0.045	5	72	49.88	15	1.8
11	0.090	10	72	56.17	10	1.6
12	0.135	15	72	63.00	6	3.4
13	0.009	1	96	31.40	34	2.1
14	0.045	5	96	51.95	14	1.9
15	0.090	10	96	65.12	14	1.6
16	0.135	15	96	85.00	8	1.6

Solvent mixture: MEK/DCM (3:1, molar ratio); temperature: 65 °C; St : (0.90 g);
(St+MAI)/solvent mixture: 20 wt.%

Table 2. Block copolymerization of methyl methacrylate with PDM-MAI.

Run No.	PDM-MAI (g)	PDM-MAI (wt.% to St)	Reaction Time (h)	Yield (wt.%)	$\bar{M}_n \times 10^3$ (g/mol)	$\bar{M}_w/\bar{M}_n$
17	0.009	1	24	72.92	44	1.6
18	0.046	5	24	74.28	22	1.7
19	0.093	10	24	57.39	18	1.6
20	0.140	15	24	51.61	16	1.5
21	0.009	1	48	80.91	41	1.7
22	0.046	5	48	82.73	22	1.9
23	0.093	10	48	63.92	17	1.6
24	0.140	15	48	56.94	16	1.6
25	0.009	1	72	91.85	43	1.7
26	0.046	5	72	85.80	19	2.0
27	0.093	10	72	84.57	14	2.0
28	0.140	15	72	69.71	13	1.8
29	0.009	1	96	92.72	42	1.7
30	0.046	5	96	99.78	17	2.2
31	0.093	10	96	74.10	12	1.7
32	0.140	15	96	66.23	13	2.4

Solvent mixture: MEK/DCM (3:1, molar ratio); temperature: 65 °C; MMA : (0.93 g);
(MMA+MAI)/solvent mixture: 20 wt.%

The ^{1}H-NMR spectrum of PDMS-*b*-PSt shown in Figure 4 is useful for the estimation of siloxane contents in mol % by determining the peak areas of the phenyl protons in PSt, and the dimethylsiloxy protons in the siloxane segment. The absorbtion ratio of the $-OSi(C\underline{H}_3)_2-$ (0.06 ppm) and $-CC_6\underline{H}_5$ (6-7

651

ppm) peaks in the spectrum indicates that the PDMS content is about 0.4 mol % for PDMS-*b*-PSt (Run No. 2, Table 1). The characteristic peaks of both PDMS and PMMA segments are observed in the ^{1}H-NMR spectrum of PDMS-*b*-PMMA (Figure 5). The methoxy, methylene, and methyl protons at 3.56, 1.86-1.78, and 0.99-0.81 ppm, respectively, are due to the PMMA segments, and the sharp singlet at 0.032 ppm is due to the PDMS segment protons. A comparison of the -OSi(C$\underline{H}_3$)$_2$- and -OC$\underline{H}_3$- absorption ratios in the ^{1}H-NMR spectrum reveals that the siloxane content of PDMS-*b*-PMMA is 0.25 mol % (Run No. 18, Table 2).
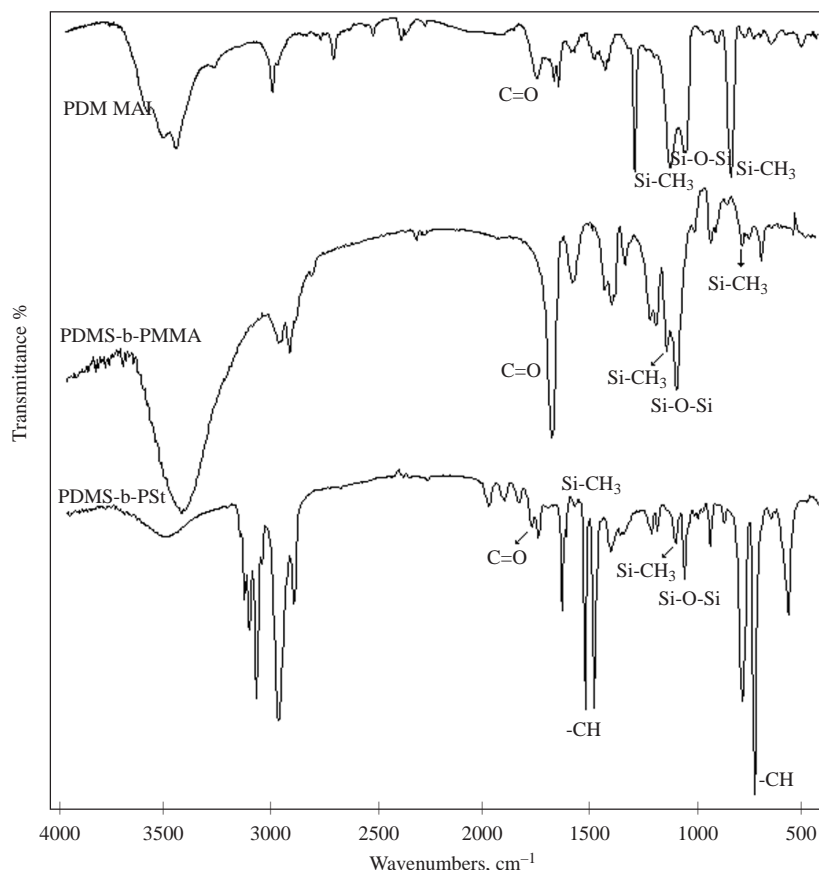
Figure 3. The FTIR spectra of block copolymers by using PDM-MAI (Run no: 15 and 32, Tables 1 and 2).
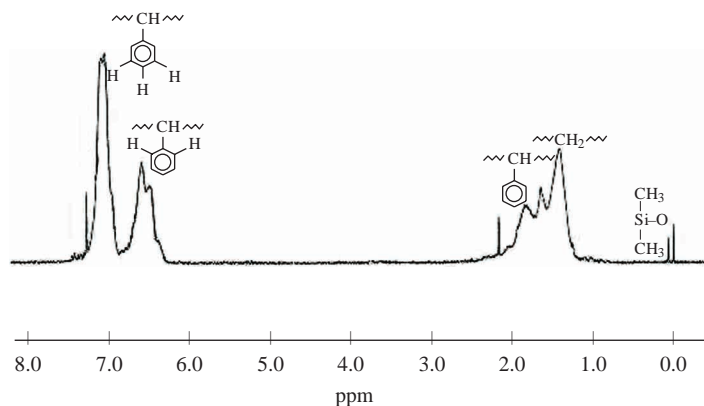
Figure 4. ^{1}H-NMR spectrum of PDMS-*b*-PSt (Run No. 2, Table 1).
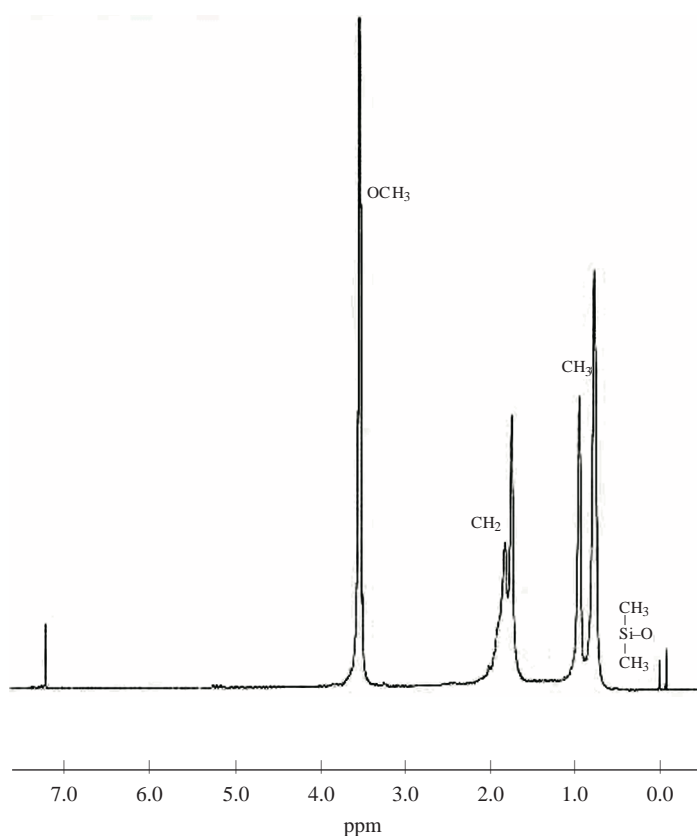
Figure 5. ^{1}H-NMR spectrum of PDMS-*b*-PMMA (Run No. 18, Table 2).

The weight loss curve of PDMS-*b*-PSt (Run No. 2, Table 1) shown in Figure 6 is obtained at a heating rate of 10 °C/min under nitrogen atmosphere. Similar weight loss curves were obtained with the other PSt copolymers synthesized but they are not given here. The TGA curve of PDMS-*b*-PSt displays one main reaction stage, which is reflected in one peak in the DTA curve. The maximum temperatures of degradation for this polymer are observed at 417 °C. The thermal behaviors of PDMS-*b*-PMMA copolymers were similar to that of PDMS-*b*-PSt. The maximum temperature of degradation for PDMS-*b*-PMMA copolymer is observed at 397 °C (Run No. 18, Table 2).
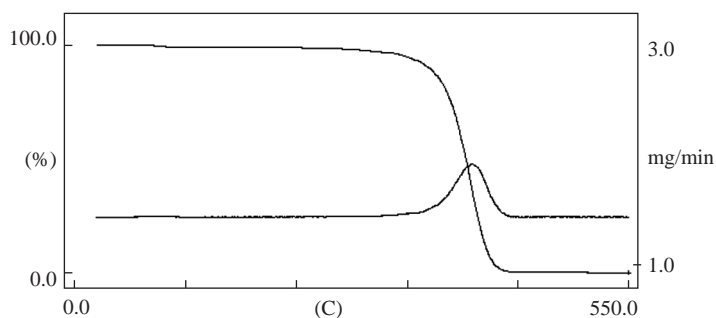
Figure 6. TGA curve of PDMS-*b*-PSt (Run No. 2, Table 1).

The glass transition temperatures (T_gs) of block copolymers were determined by DSC measurement, taken at the onset of the corresponding heat capacity jump. Only one T_g value could be observed at around 98 °C for the PDMS-*b*-PSt copolymer (Figure 7) and at around 104 °C for the PDMS-*b*-PMMA copolymers.

The T_g of the PDMS component cannot be observed due to lower PDMS block lengths with respect to the PSt component in copolymers. However, the T_g value of PSt, because of the plasticizer effect of PDMS, is slightly lower than the T_g value of homo-PSt (100 °C) [17].
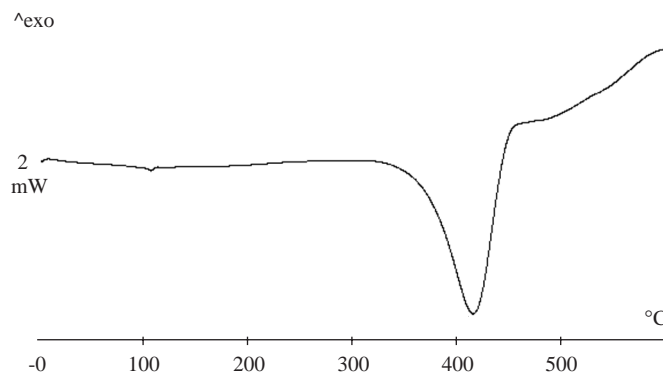
Figure 7. DSC thermogram of PDMS-*b*-PSt (Run No. 2, Table 2).

Tables 1 and 2 show that the yields of PDMS-*b*-PMMA copolymers are higher than those of PDMS-*b*-PSt copolymers under the same reaction conditions due to the overall consumption of MMA being higher than that of St resulting from a higher propagation rate ($k_{p,MMA}$ = 573 mol/L.s; $k_{p,St}$ = 176 mol/L.s)[25].
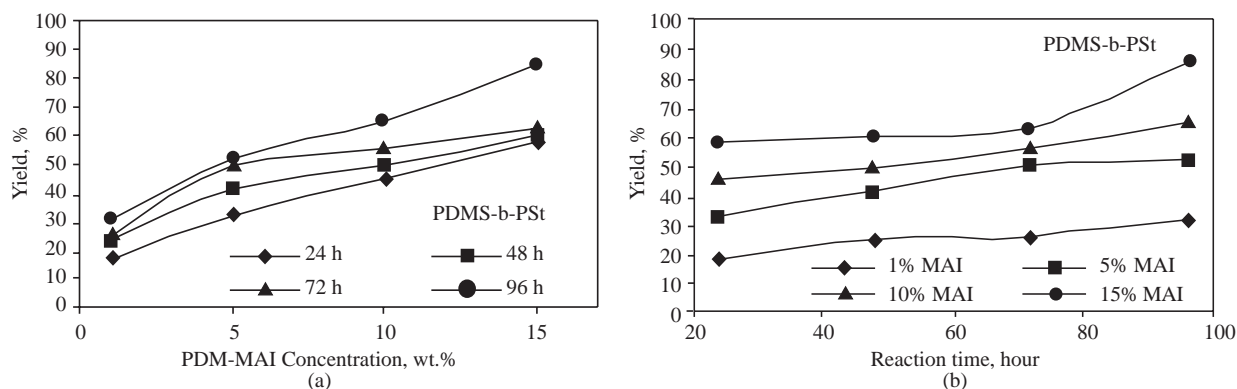
Figure 8. The yields of PDMS-b-PSt block copolymers as functions of (a) initial wt.% of PDM-MAI to St, and (b) reaction time.

PDM-MAI was found to behave as a polyazo-initiator with high polymerization activity, comparable to that of AIBN, as expected from the results of various authors[2,12]. When the block copolymer yields are compared on the basis of macroazoinitiator concentrations, the PDMS-*b*-PSt copolymer yields increase with increasing PDM-MAI concentration (Figure 8a). On the other hand, the PDMS-*b*-PMMA copolymer yields decrease with increasing PDM-MAI concentration, which may be due to radical pairs forming after the scission of the polyazo-initiator tending to recombine due to the slow diffusion rate (Figure 9a). The effects of reaction time on yields are given in Figures 8b and 9b. The yields of both PDMS-*b*-PSt and PDMS-*b*-PMMA copolymers tend to increase with increasing reaction time.
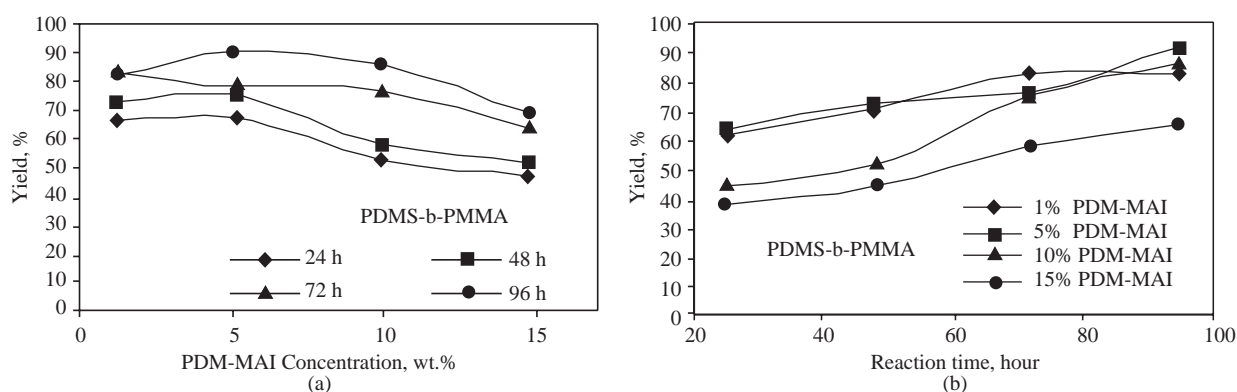
Figure 9. The yields of PDMS-b-PMMA block copolymers as functions of (a) initial wt.% of PDM-MAI to MMA, and (b) reaction time.

As expected, the number-average molecular weights of both block copolymers decrease with increases in macroazoinitiator to a monomer initial percentage ratio for most of the reaction times (Figures 10a and b).
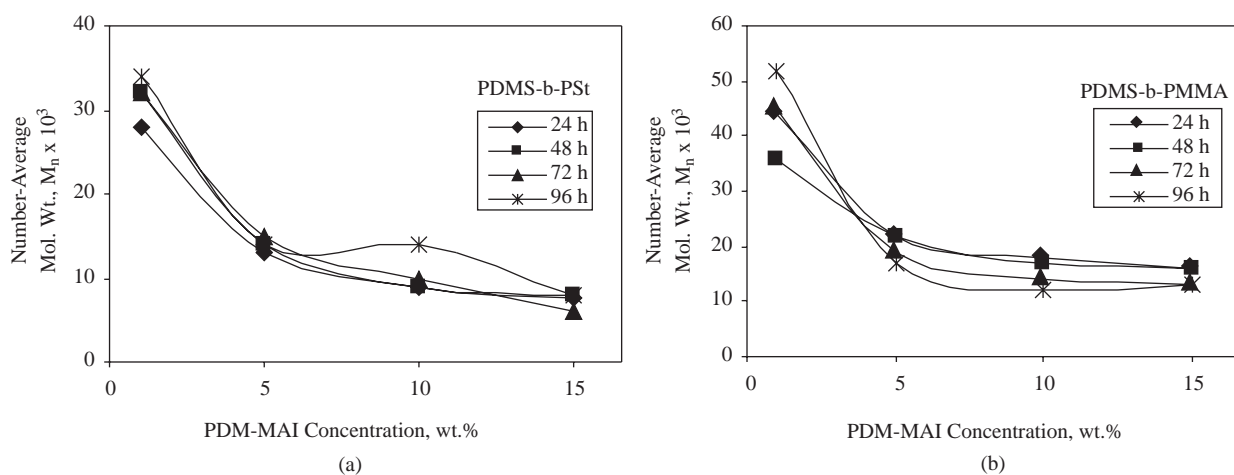

Figure 10. Number-average molecular weights of (a) PDMS-b-PSt, and (b) PDMS-b-PMMA copolymers as functions of initial wt.% of PDM-MAI to St and MMA, respectively.

Figures 11a and b show that reaction time has a negligible effect on the number-average molecular weights of block copolymers. The slight decrease in the molecular weights of PDMS-*b*-PMMA copolymers, and the slight increase in the molecular weights of PDMS-*b*-PSt copolymers with increases in reaction time can be attributed to different termination mechanisms[23]. According to the termination mechanism, the block copolymerization of MMA should produce mainly AB-type block copolymer, but if the added monomer tends to terminate via recombination such as with styrene, block copolymers are the ABA-type. The relatively higher molecular weights of PDMS-b-PMMA copolymers under the same reaction conditions are attributed to the higher propagation rate of MMA[25].
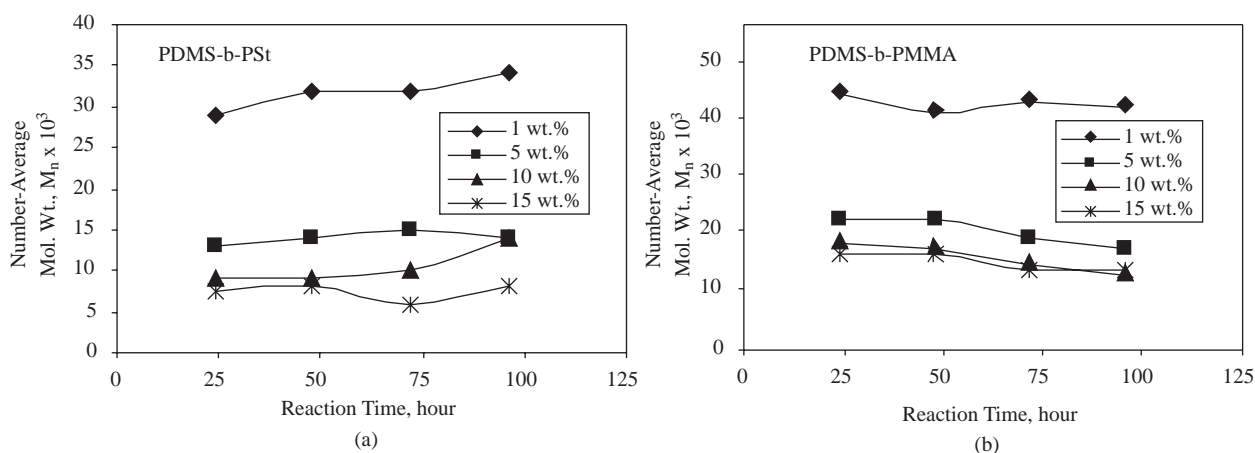
Figure 11. Number-average molecular weights of (a) PDMS-b-PSt, and (b) PDMS-b-PMMA copolymers as functions of reaction time using PDM-MAI with different initial weight percentages.

Conclusion

Not only polysiloxane(azobiscyanopentanamide)s (PASAs) with different siloxane chain lengths[15,17,18]but also hydroxybutyl-terminated PDMS-ACP macroazoinitiators[19] of varying molecular weights were already reported to be effective radical polyazo-initiators for typical vinyl monomers comparable to AIBN. In this study, a polydimethylsiloxane based macroazoinitiator (PDM-MAI, $\bar{M}_n$ = 812 g/mol) having labile azo groups and dimethylsiloxane segments was synthesized and characterized. PDM-MAI was used to initiate the radical block copolymerization of both St and MMA. PDM-MAI was found to behave as a polyazo-initiator for the radical polymerizations of St and MMA. FTIR analysis showed that PDMS segments are present in the block copolymer structures. The polydispersities of both block copolymers were mostly in the range 1.5-2.0. The yields of poly(dimethylsiloxane-b-methyl methacrylate) (PDMS-*b*-PMMA) block copolymers were slightly higher than those of poly(dimethylsiloxane-b-styrene) (PDMS-*b*-PSt) block copolymers under the same reaction conditions. It was observed that all the block copolymer yields increased with an increase in the reaction time. Moreover, increasing percentages of PDM-MAI to monomer in the starting reaction mixture provided a slight decrease in the number-average molecular weights of PDMS-*b*-PMMA copolymers, but a slight increase in the number-average molecular weights of PDMS-*b*-PSt copolymers. The slight decrease in molecular weights of PDMS-*b*-PMMA copolymers and the slight increase in molecular weights of PDMS-*b*-PSt copolymers with the increase in reaction time could be attributed to the different termination mechanisms.

Acknowledgments

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