

Synthesis of Poly(octadecyl acrylate-*b*-styrene-*b*-octadecyl acrylate) Triblock Copolymer by Atom Transfer Radical Polymerization

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ABSTRACT: The synthesis of triblock copolymer poly(octadecyl acrylate-*b*-styrene-*b*-octadecyl acrylate), using atom transfer radical polymerization (ATRP), is reported. The copolymers were prepared in two steps. First, polystyrene was synthesized by ATRP using α, α' -dichloro-*p*-xylene/CuBr/bpy as the initiating system; Second, polystyrene was further used as macroinitiator for the ATRP of octadecyl acrylate to prepare ABA triblock copolymers in the presence of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{PPh}_3$ in toluene. Polymers with controlled molecular weight ($M_n = 17,000\text{--}23,400$) and low polydispersity index value (1.33–1.44) were obtained. The relationship between molecular weight versus conversion

showed a straight line. The effect of reaction temperature on polymerization was also investigated, showing a faster polymerization rate under higher temperature. The copolymers were characterized by FTIR, $^1\text{H-NMR}$, DSC, and GPC and the crystallization behavior of the copolymers was also studied. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1539–1545, 2004

Key words: octadecyl acrylate; synthesis; atom transfer radical polymerization (ATRP); triblock copolymer; crystallization

INTRODUCTION

Copolymers of poly(octadecyl acrylate) (PODA), containing a C18 long side chain, have been extensively studied because of their interesting bulk and solution properties. An outstanding feature is the liquid-crystal and thermochromic properties.^{1–6} Moreover, the biphasic structure of comblike poly(octadecyl acrylate) gives rise to unique transport properties,^{7–9} which make it attractive to mimic barrier synthetic composites and biological structures related to the permeation processes. In addition, copolymers containing ODA show shape memory behaviors attributed to a reversible order–disorder transition associated with the interaction between the alkyl side chains of ODA units.^{10–12} The structural parameters of macromolecules (e.g., chain length, polydispersity, architecture, sequence distribution) play an important role in the performance of the polymer materials. Although acrylates can be polymerized anionically, the preparation of well-defined polymers is hindered by a number of side reactions.¹³ Several works have been reported

to overcome this problem.^{14,15} However, because of the starved reaction conditions needed in anionic polymerization, most commercially available polyacrylates are still manufactured by free-radical polymerization. However, conventional radical polymerization of ODA usually yielded polymers with wide molecular weight distributions and poorly controlled structure.^{5,16,17} Therefore, we seek to develop a living polymerization method to prepare well-defined (co)polymers with poly(octadecyl acrylate).

Compared with traditional methods, living/controlled radical polymerization, providing polymers with controlled molecular weight and narrow molecular weight distributions and with various architectures, is easier to carry out and have considerably widened the opportunities for (co)polymer synthesis. Tremendous progress has been made in the past few years, particularly in the areas of the following: (1) nitroxide-mediated free-radical polymerization,^{18–20} which uses stable nitroxyl radicals; (2) reversible addition fragmentation chain transfer (RAFT) process,^{21–24} which is carried out in the presence of dithioesters together with a free-radical initiator; and (3) atom transfer radical polymerization (ATRP),^{25–29} which uses various transition metal complexes.

We successfully carried out the RAFT polymerization of ODA in benzene solution, using 2-cyanoprop-2-yl dithiobenzoate as RAFT agent.³⁰ In this article, we report our work on the ATRP synthesis of ABA

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TABLE I
Synthesis of Difunctional Macroinitiators by ATRP^a

Sample	Macroinitiator	Catalyst	Monomer/DCX	Temperature (°C)	Time (h)	$M_{n, GPC}$	M_w/M_n
1	PODA	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{PPh}_3$	100/1	120	29.5	14,200	1.81
2	PSt	CuBr/bpy	100/1	100	6	8,300	1.44
3	PSt	CuBr/bpy	150/1	100	17	15,200	1.20

^a Conditions: $[\text{DCX}]_0 : [\text{CuBr}]_0 : [\text{bpy}]_0 = [\text{DCX}]_0 : [\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]_0 : [\text{PPh}_3]_0 = 1 : 1 : 3$.

triblock copolymers of poly(octadecyl acrylate) using the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{PPh}_3$ catalyst system, which is attractive because of its low price and the nontoxic nature of iron. The effects of polymerization temperature, monomer/initiator ratio, and molecular weight of macroinitiator are also examined.

EXPERIMENTAL

Materials

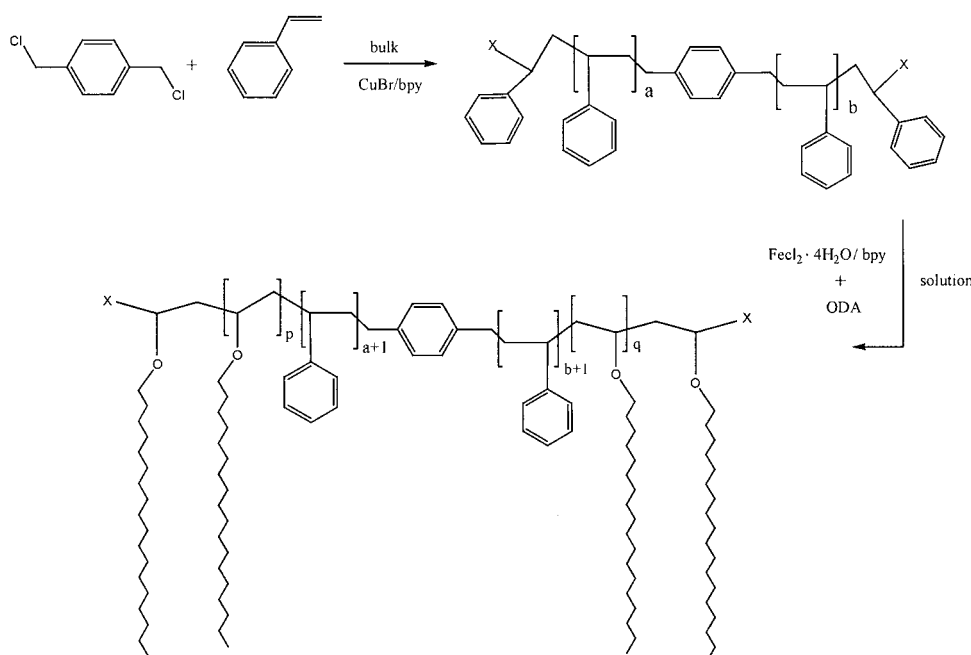
ODA (Research Center of the Beijing Eastern Chemical Works, Beijing, China) was purified by distillation under reduced pressure. Styrene (CP, Shanghai Chemical Reagent Co., China) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with water and drying with sodium sulfate anhydrous overnight, and finally distilled under vacuum. Copper (I) bromide (CuBr; CP, Shanghai Chemical Reagent Co.) was purified by washing with acetic acid and acetone, then dried under vacuum. α, α' -Dichloro-*p*-xylene (DCX; CP, Shanghai Chemical Reagent Co.) was recrystallized twice

with ethanol. Triphenylphosphine (CP, Shanghai Chemical Reagent Co.) was recrystallized with anhydrous alcohol. Toluene [analytical reagent (AR), Shanghai Chemical Reagent Co.] was purified by distilling under vacuum. 2,2'-Bipyridine (bpy; AR, Shanghai Chemical Reagent Co.), tetrahydrofuran (THF; AR, Shanghai Chemical Reagent Co.), hydrochloric acid (HCl; AR, Jiangsu Jincheng Chemical Reagent Co.), and methanol (commercially available) were used as received.

Synthetic procedures

Synthesis of difunctional PSt macroinitiators

A dry one-neck, round-bottom flask was filled with St, DCX, CuBr, and bpy. Three freeze-pump-thaw cycles were performed, and the flask was sealed under vacuum and placed in an oil bath heated at the desired temperature to initiate the polymerization. The polymerization was stopped at a desired time by cooling the tubes in ice water. Afterward, the flask was opened and the contents were dissolved in THF, pre-



Scheme 1 Synthesis of PODA-PSt-PODA triblock copolymer by ATRP (X = Cl or Br).

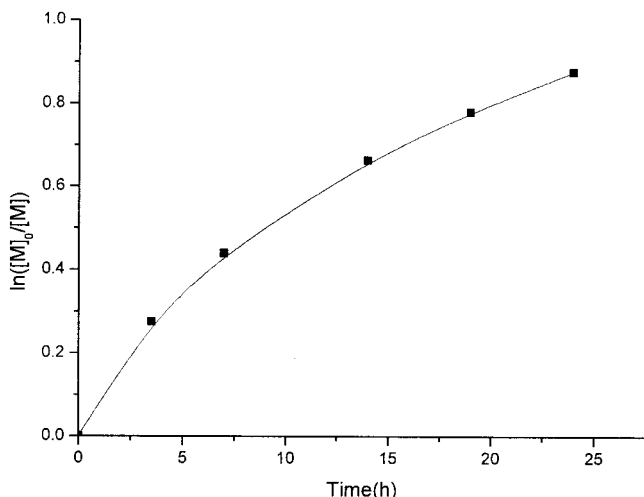


Figure 1 Dependency of $\ln([M]_0/[M])$ on time in the copolymerization of PODA-PSt-PODA in toluene at 120°C. Conditions: $[ODA]_0 : [\text{macroinitiator}]_0 : [\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]_0 : [\text{PPh}_3]_0 = 50 : 1 : 2 : 4$; $M_{n,\text{GPC}}(\text{X-PSt-X}) = 15,200$; $M_w/M_n(\text{PDI}) = 1.20$; $\text{ODA}/\text{toluene} = 2 : 1$ (w/w).

cipitated into a large amount of methanol for more than 3 days, and then filtered, washed, and dried under vacuum. The polymer was purified by redissolving in THF and reprecipitating in methanol three times.

Synthesis of triblock copolymers

The procedure was the same as discussed in the previous section except that a macroinitiator (X-PSt-X) and solvent (toluene) were initially added to the flask. Once the macroinitiator was dissolved completely, the monomer (ODA), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and PPh_3 were added.

Three freeze-pump-thaw cycles were performed, the flask was sealed under vacuum, and then the flask was immersed in an oil bath at the desired temperature to start the polymerization. Samples were taken at regular intervals and the polymer was purified as described above.

Analysis and measurements

Conversion of monomer was determined by gravimetry. Molecular weight and its distribution were measured using a Waters 1515 GPC apparatus (Waters, Milford, MA) with THF as the mobile phase and a column temperature of 30°C. Polystyrene standards were used to calibrate the columns. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 with an INOVA 400-MHz spectrometer (Varian Associates, Palo Alto, CA) at ambient temperature. FTIR was measured using a Nicolet Avatar 360 spectrometer (Nicolet Analytical Instruments, Madison, WI). Differential scanning calorimetry (DSC) measurement was processed using a TA Instruments (New Castle, DE) DSC 2010 at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of difunctional macroinitiators

Difunctional macroinitiators were prepared by bulk ATRP of styrene in the presence of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{PPh}_3$ or CuBr/bpy with DCX as the initiator. The experimental molecular weights and molecular weight distribution of the macroinitiators are listed in Table I. Besides PSt, we also used PODA (sample 1 in Table I) as a macroinitiator to carry out ATRP, but with $[\text{St}]_0 : [\text{Cl-PODA-Cl}]_0 : [\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]_0 : [\text{PPh}_3]_0 = 300 : 1 : 2 :$

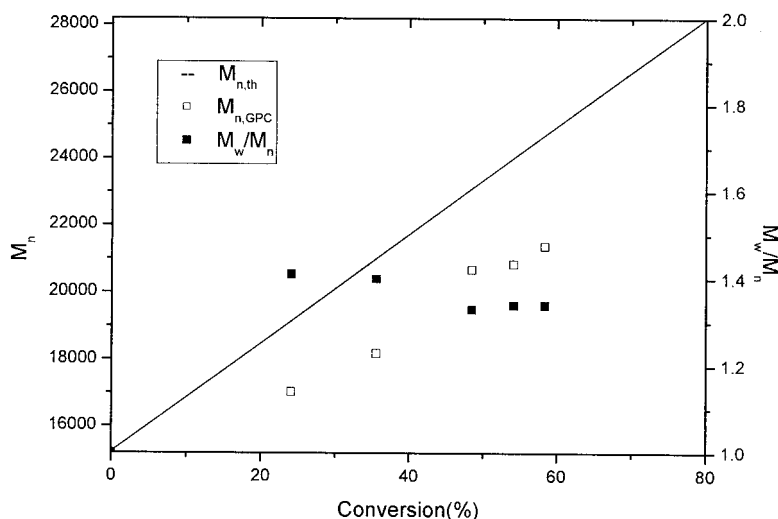


Figure 2 Dependency of M_n and M_w/M_n on conversion in the copolymerization of PODA-PSt-PODA in toluene at 120°C. Conditions are identical to those in Figure 1.

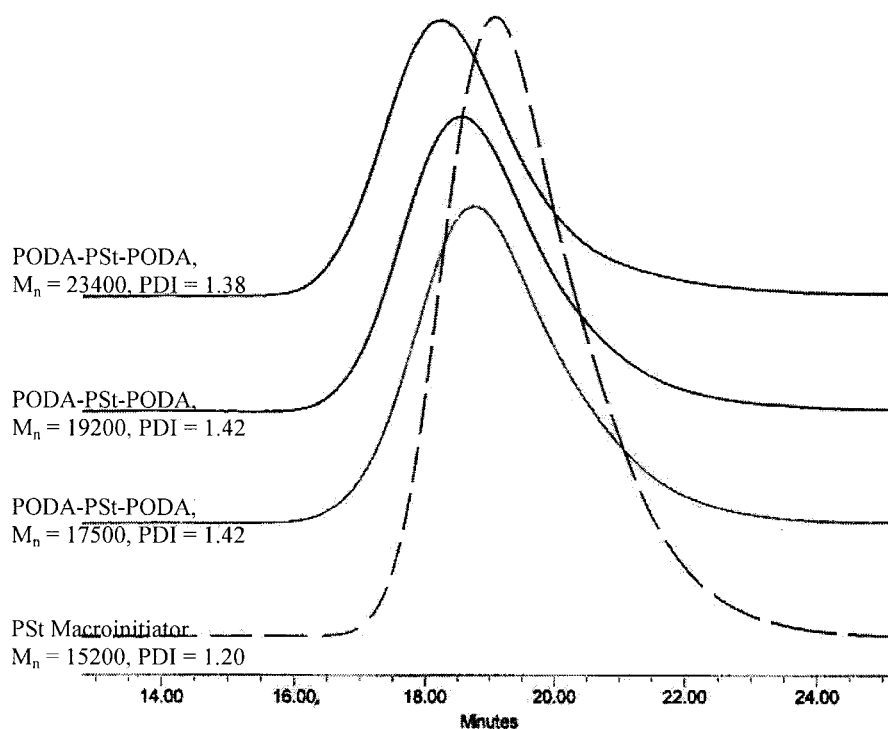


Figure 3 GPC traces of macroinitiator and the produced block copolymers.

4, we obtained the copolymer ($M_{n,GPC} = 15,200$, $M_w/M_n = 1.67$) with a conversion of 0.3% after 118 h at 80°C, the result of which was disappointing.

Synthesis of PODA-PSt-PODA triblock copolymer

Triblock copolymer PODA-PSt-PODA was synthesized by ATRP of ODA, using PSt as the macroinitiator and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{PPh}_3$ as the catalyst in toluene. PSt macroinitiator was obtained by homopolymerization of St using a difunctional initiator DCX (Scheme 1). It is well known that within the mixed halide system (e.g., R-Br/CuCl), a mixture of both bromine and chlorine atoms caps the polymer chain during the polymerization.^{28,29,31,32} So here in this article, X (X = Cl or Br) was used to represent the halogen chain end.

The kinetic plot of $\ln([M]_0/[M])$ versus time of the triblock copolymerization of PODA-PSt-PODA at 120°C and evolution of M_n and M_w/M_n with monomer conversion are presented in Figure 1 and Figure 2, respectively. The semilogarithmic kinetic plot shows deviation from linear, indicating the existence of some chain transfer and termination reactions. M_n of PODA-PSt-PODA, determined by GPC, increased with increasing conversion, and the polydispersity index (PDI, or M_w/M_n) value varied from 1.33 to 1.41. The deviation of the $M_{n,GPC}$ with $M_{n,gravimeter}$ may be attributable to the difference in hydrodynamic volumes between triblock copolymers and polystyrene standards.

The polymers obtained were characterized by GPC. Results showed that the molecular weight of copolymer increased after the polymerization. The monomodal shape of the GPC trace of the obtained polymer suggests the formation of block copolymer without homopolymerization. The GPC traces shifted entirely to high molecular weight as shown in the overlaid traces of starting material and copolymers (Fig. 3).

Influence of temperature

The influence of polymerization temperature on the copolymerization was investigated and the results are shown in Table II (samples 1–10). As expected, polymerization at 120°C is a little faster than that under 100°C, if other polymerization conditions are the same. For example, with the same polymerization time of 9 h (samples 2 and 8), conversion (32.7%) at 120°C is higher than that (29.4%) at 100°C. Dependency of M_n and M_w/M_n on conversion under these conditions is also listed in Table II. Results show that M_n increases with increasing conversion and the value of PDI varies from 1.38 to 1.43.

Sample 2 in Table I was also used to synthesize PODA-PSt-PODA triblock copolymers. Results are listed in Table II (from sample 11 to sample 15). It is clear that conversion increases with time and molecular weight increases with conversion. However, the PDI of these polymers is a little higher (1.55–1.89),

TABLE II
Data for PODA-PSt-PODA Triblock Copolymer Synthesis^a

Sample	$M_{n,\text{macroinitiator}}/$ M_w/M_n	Temperature (°C)	Time (h)	Conversion (%)	$M_{n,\text{GPC}}$	M_w/M_n
1	15,200/1.20	100	4.5	18.6	17,500	1.42
2			9	29.4	18,900	1.44
3			16.5	40.3	19,200	1.42
4			21.5	42.2	21,000	1.42
5			90	63.7	23,400	1.38
6	15,200/1.20	120	3.5	12.7	17,000	1.40
7			6	20	17,400	1.43
8			9	32.7	19,100	1.41
9			18.5	47.0	20,300	1.39
10			88	64.9	22,000	1.39
11	8300/1.44	100	4	6.6	10,100	1.62
12			7.5	12.4	10,800	1.69
13			14	20.1	12,000	1.86
14			19	26.6	12,600	1.89
15			96	75.9	19,100	1.55

^a Conditions: $[\text{ODA}]_0 : [\text{macroinitiator}]_0 : [\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]_0 : [\text{PPh}_3]_0 = 100 : 1 : 2 : 4$; ODA/toluene = 2 : 1 (w/w).

which may be a consequence of the high polydispersities (1.44) of the starting macroinitiator.

Analysis of PODA-PSt-PODA triblock copolymer

Formation of the copolymer was also supported by FTIR analysis (Fig. 4). The spectra showed the C—H stretching ($\nu = 3000\text{--}3100\text{ cm}^{-1}$) in the phenyl groups and a carbonyl peak was observed at $\nu = 1736\text{ cm}^{-1}$, corresponding to the carbonyl stretching from acrylate groups, indicating the successful copolymerization of ODA and St.

The ¹H-NMR spectrum of PODA-PSt-PODA triblock copolymer is shown in Figure 5. The signals at

4.0 ppm correspond to the methylenes of the ester group of ODA, and the peaks at 6.6 and 7.1 ppm can be assigned to the aromatic protons in the styrene units. On the basis of the ratio of the area of the two peaks and the molar mass of Cl-PSt-Cl, the composition of block copolymer was calculated, which gives a molecular weight, $M_{n,\text{NMR}} = 25,700$, greater than that from GPC, $M_{n,\text{GPC}} = 19,200$, but close to the theoretical value, $M_{n,\text{theor}} = 24,600$.

The DSC curve of PODA-PSt-PODA is shown in Figure 6. A significant endothermic peak can be seen at 43.19°C, indicating that the copolymer has some crystalline morphology. Extensive studies of the phys-

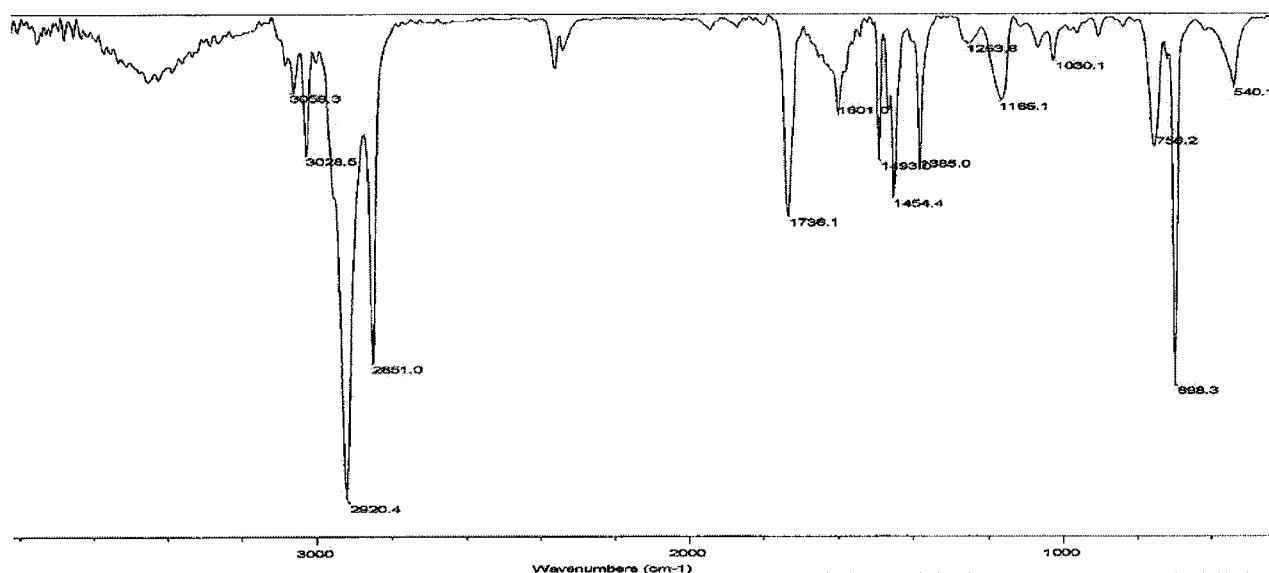


Figure 4 FTIR spectrum of PODA-PSt-PODA prepared by ATRP.

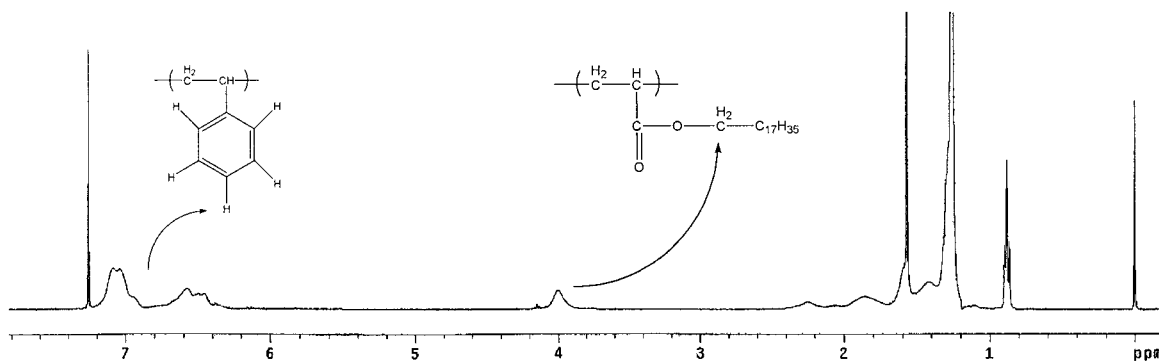


Figure 5 $^1\text{H-NMR}$ spectrum of PODA-PSt-PODA prepared by ATRP.

ical, thermal, and structural properties of polymers with long side chain were previously reported.¹⁻⁵ For the first time, we examined the relationship between the polydispersity and the thermal properties of these polymers,³⁰ and found that that PODA obtained from living polymerization has a greater crystallinity than that polymerized by conventional polymerization. Here, the degree of crystallinity (χ_c) of copolymers containing different concentrations of ODA units is summarized in Table III. The melting point (T_m) and heat of fusion (ΔH_m) were determined from the endothermic peaks. The degree of crystallinity was calculated from the following:

$$\chi_c = \frac{(\Delta H_f)}{(\Delta H_{f0})} \quad (1)$$

where ΔH_f was measured by DSC (expressed in J/g of sample) and the value of ΔH_{f0} is 219.5 J/g of crystal.^{1,33} This value was taken from studies of the melting behavior of long chain *n*-alkanes that exhibit a hexagonal crystal structure. It is well accepted that long side-chain polyacrylates crystallize into such a lattice.

From Table III, we can see that the crystallization is reduced by the incorporation of the St unit, and with the increase of the concentration of ODA units, the degree of crystallinity (χ_c) of copolymers increases. In addition, there is a slight increase of the melt enthalpy of ODA with increasing concentration of ODA units. This phenomenon may be attributed to the fact that the crystallization is a consequence of the alkyl long side chains of ODA and not of the main chain.

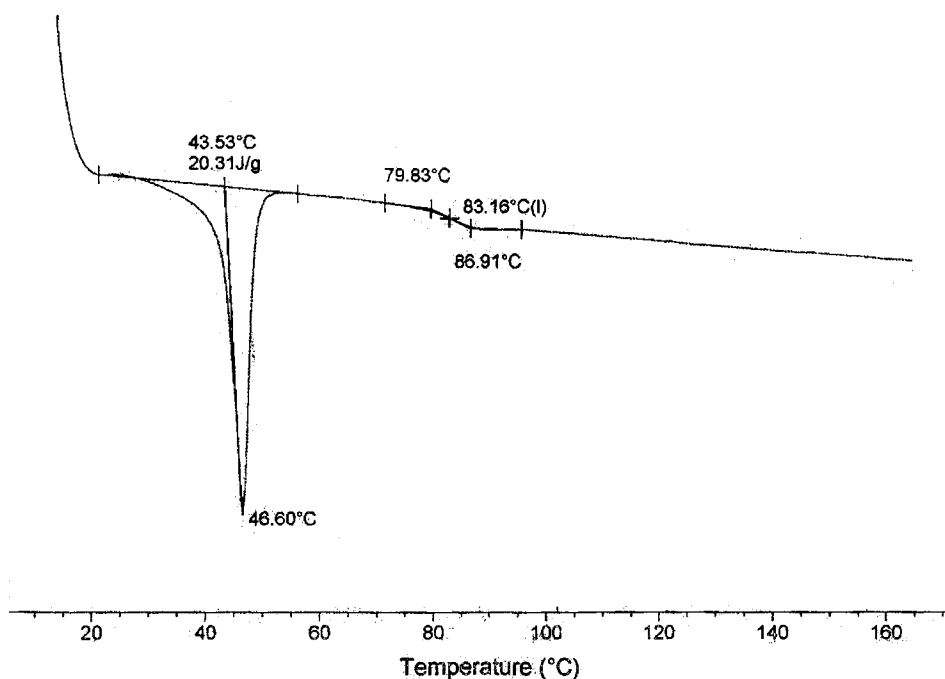


Figure 6 DSC curve of PODA-PSt-PODA ($M_{n,GPC} = 10,100$; PDI = 1.62).

TABLE III
Thermal and Physical Properties of PODA-PSt-PODA

Sample	$M_{n, GPC}$	ODA (mol %)	T_m (°C)	ΔH_f (J g ⁻¹ of ODA)	χ_c
1 ^a	14,800	100	47.2	104.1	0.47
2	10,100	7.6	43.5	20.3	0.09
3	12,000	20.1	44.1	36.1	0.16
4	12,600	25.0	44.3	42.5	0.19

^a Ref. 30.

CONCLUSIONS

Triblock copolymer poly(octadecyl acrylate-*b*-styrene-*b*-octadecyl acrylate) was successfully synthesized through ATRP, catalyzed by FeCl₂·4H₂O/PPh₃ in toluene. The kinetic plot of ln([M]₀/[M]) versus time of the copolymerization shows a deviation from linear and the molecular weight increased with increasing conversion. The influence of polymerization temperature on the copolymerization was investigated; results showed that polymerization is faster at higher temperature. The crystallization behavior of the copolymers was also studied and results affirmed that the crystallinity is attributed to the octadecyl side chain and not to the main chain and, further, that the degree of crystallinity (χ_c) of copolymers increases with increasing concentration of ODA units.

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