Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Jian Zhu[a]; Xiulin Zhu[a]; Zhenping Cheng[a]; Jianmei Lu[a]; Feng Liu[a]
[a] School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, China

To cite this Article Zhu, Jian , Zhu, Xiulin , Cheng, Zhenping , Lu, Jianmei and Liu, Feng(2003) 'Reversible Addition-Fragmentation Chain-Transfer Polymerization of Octadecyl Acrylate', Journal of Macromolecular Science, Part A, 40: 9, 963 — 975

To link to this Article: DOI: 10.1081/MA-120023530
URL: http://dx.doi.org/10.1081/MA-120023530

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 9, pp. 963–975, 2003

Reversible Addition–Fragmentation Chain-Transfer Polymerization of Octadecyl Acrylate

Jian Zhu, Xiulin Zhu,* Zhenping Cheng, Jianmei Lu, and Feng Liu

School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, China

ABSTRACT

Polymerization of octadecyl acrylate (ODA) was carried out in benzene solution using the 2-cyanoprop-2-yl dithiobenzoate (CPDB) as the reversible addition–fragmentation chain-transfer (RAFT) agent and AIBN as the initiator. The results show the obtained polymer with controlled molecular weight and low PDI value. The relationships between both of the $\ln([M_0]/[M])$ vs. reaction time and molecular weight vs. conversion showed a straight line. The block copolymer of ODA and styrene (PODA-*b*-PSt) obtained using poly(octadecyl acrylate) (PODA) as a macro-RAFT agent. The polymers were characterized by ^{1}H NMR, DSC, and gel permeation chromatograph (GPC). The effect of molar ratio [CPDB] : [AIBN] and reaction temperature on polymerization was investigated.

Key Words: 2-Cyanoprop-2-yl dithiobenzoate; Octadecyl acrylate; Reversible addition–fragmentation chain-transfer (RAFT) polymerization.

INTRODUCTION

Homopolymers of long side chain alkyl acrylates and methacrylates and their copolymers with ethylene, vinyl acetate, etc. are used extensively as pour-point depressants and flow improvers in high waxy crude oils, lubricating oils, and fuel oils.[1,2] Octadecyl

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*Correspondence: Xiulin Zhu, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, 215006, China; Fax: +86-512-65112796; E-mail: xlzhu@suda.edu.cn.

DOI: 10.1081/MA-120023530
1060-1325 (Print); 1520-5738 (Online)
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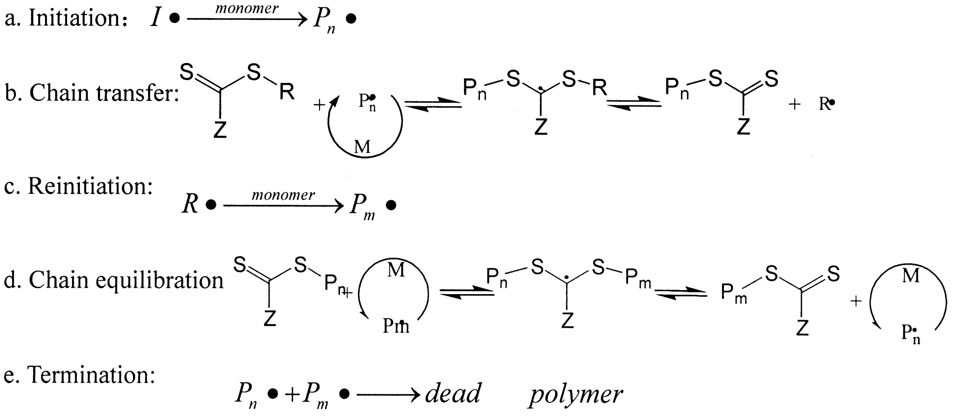
acrylate (ODA) is used extensively in the preparation of these additives. The molecular weight and polydispersity of the polymers are important in the performance of these additives, particularly for crude oils.[3] Although acrylates can be polymerized anionically, the preparation of well-defined polymers is hindered by a number of side reactions.[4] Several works have been reported to overcome this problem.[5,6] But due to the starve reaction conditions; most commercially available poly-acrylates are still manufactured by free-radical polymerization. However, in comparison with ionic polymerization, free-radical polymerization is difficult to control the molecular weight and polydispersity of resulting polymer.

Recently, living/controlled free-radical polymerization has attracted the attention of polymer chemists as a versatile chemistry enabling the synthesis of a wide range of tailor-made polymers with predetermined degrees of polymerization and narrow polydispersity. Tremendous progress has been made,[7] particularly in the areas of following: (1) nitroxidemediated free-radical polymerization,[8–10] which utilizes stable nitroxyl radicals; (2) atom transfer radical polymerization (ATRP),[11–13] using various transition metal complexes; and (3) reversible addition–fragmentation chain-transfer (RAFT) process,[14–18] which is carried out in the presence of dithioesters together with a free-radical initiator.

Among the preceding free-radical polymerization techniques, RAFT presents some advantages. These include the ease of the polymerization procedure, effective for a wide range of monomers including functional monomers containing acid,[19] hydroxy, amino groups[20] and the fact that the prepared polymers contain no impurities such as transition metals. Reversible addition–fragmentation chain-transfer leads to polymeric materials with controlled molecular weight, narrow distribution, and well-defined architecture (block copolymers,[21] graft polymers,[22] star polymers,[17] etc.). The mechanism of the RAFT process is shown in Sch. 1.

In this process, initiator-derived primary radicals [I$^\bullet$] react with monomer units [M] to form oligomeric radicals [R$^\bullet$], which undergo addition to the C=S of the dithioester chain transfer agents. The resulting species then loses the group P, a good hemolytic leaving group, as a radical capable of initiating a polymerization reaction or propagating



Scheme 1. Mechanism of RAFT reaction.

further. Equilibrium is then established between active (propagating) and dormant polymer chains via the addition (rate coefficient k_{add}) and fragmentation (rate coefficient $k_{-\mathrm{add}}$) steps.

In this paper, we report the RAFT polymerization of ODA in benzene solution, using 2-cyanoprop-2-yl dithiobenzoate (CPDB) as RAFT agent, for the first time.

EXPERIMENTAL

Materials

Octadecyl acrylate was purchased from the Research Center of the Beijing Eastern Chemical Works (Beijing, China) and purified by distillation under reduced pressure. 2,2′-Azoisobutyronitrile (AIBN, Shanghai Chemical Reagent Co. Ltd, 98%), was recrystallized from ethanol and kept in a refrigerator under 4°C. 2-Cyanoprop-2-yl dithiobenzoate was synthesized according to Ref.[23]. Benzyl chloride reacted with sulfur and sodium methoxide in methanol to prepare dithiobenzoic acid. Bis(dithiobenzoate) disulfide was obtained by the reaction of dithiobenzoic acid with dimethyl sulfoxide (DMSO) in ethyl acetate at 65°C for 10 h in the dark. 2-Cyanoprop-2yl dithiobenzoate was synthesized by the reaction of bis(dithiobenzoate) with AIBN in ethyl acetate at 70°C for 15 h and then purified by means of column chromatography on silica oxide with mixed petroleum ether and ethyl acetate as eluent. Other materials were obtained from Shanghai Chemical Reagent Co. Ltd. and used as received.

Polymerizations

A mixture of predetermined concentration of ODA, benzene, AIBN, and CPDB was added to a 1 mL amps. The system was sealed after bubbled with nitrogen for 20 min to eliminate oxygen. The seal was opened and the mixture was diluted with a little THF then precipitated in methanol, after it reacted with a predetermined time and temperature. The polymer was filtered and soluted in THF, then precipitated in methanol for times to purify the polymer. The third filtered polymer was dried at 40°C under vacuum for 48 h. The conversion was determined gravimetrically. The same procedure as RAFT polymerization of Styrene (St) was used except CPDN was substituted by poly(octadecyl acrylate) (PODA) obtained from ODA RAFT polymerization to prepare the block copolymer of PODA-*b*-PSt.

Characterization

The molecular weight (M_n) and polydispersity (PD) were measured on a Waters 1515 gel permeation chromatograph (GPC) using tetrahydrofuran as the eluent at a flow rate of 1.0 mL min^{-1}. Molecular weights were determined from standard polystyrene calibration. ^{1}H NMR spectra of the polymers were recorded on a NAVA400 nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. DSC measurement is processed using a TA instruments DSC 2010 at a heating rate of 10°C min^{-1} in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Reversible Addition–Fragmentation Chain-Transfer Polymerization of Octadecyl Acrylate

Octadecyl acrylate was polymerized in benzene solution with AIBN as an initiator catalyzed by CPDB as RAFT agent at 60°C ($[\mathrm{ODA}]_0 : [\mathrm{CPDB}]_0 : [\mathrm{AIBN}]_0 = 200 : 1 : 0.5$). The results are displayed in Figs. 1 and 2. The plot of $\ln([M_0]/[M])$ vs. time is shown in Fig. 1. A straight line is observed, indicating that the kinetics is first order with respect to the monomer and that the concentration of propagating radicals remains constant during the polymerization. An induction period of about 40 min was observed. It may be a result of the side reaction in the pre-equilibrium period. It can also be seen that the monomer conversion increases with reaction time in 14 h. In Fig. 2, the number-average molecular weight measured by GPC, $M_{n(\mathrm{GPC})}$, of the resulting PODA, rises from 9500 to 41,000 proportionally with increasing monomer conversion from 11% to 69%. A linear relationship was found that corresponds closely to the theoretical values, which can be obtained with the following formula (1):

$$M_{n,\mathrm{th}} = M_{n,\mathrm{RAFT}} + \frac{[m]_0 M_0 x}{[\mathrm{RAFT}]_0} \tag{1}$$

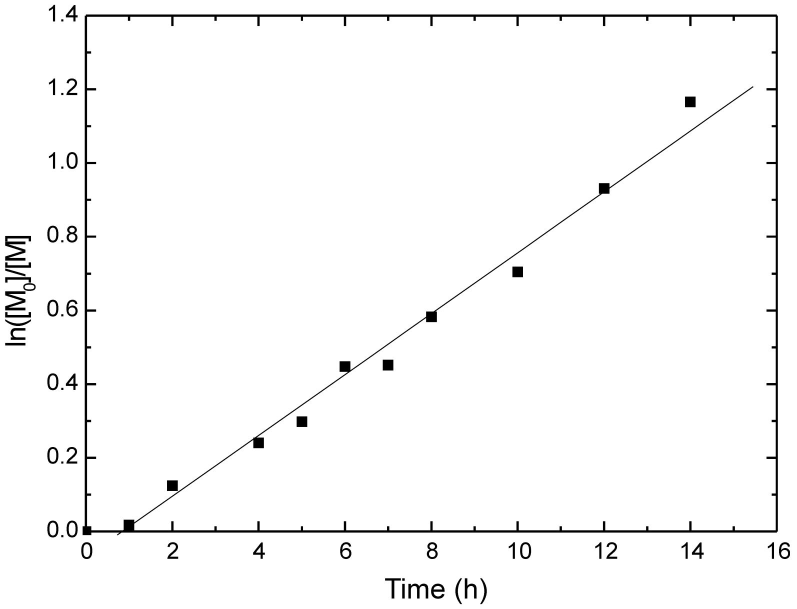


Figure 1. Kinetic plot for ODA RAFT polymerization in solution at 60°C. Conditions: $[\mathrm{ODA}]_0 : [\mathrm{CPDB}]_0 : [\mathrm{AIBN}]_0 = 200 : 1 : 0.5$, $[\mathrm{ODA}]_0 = 1.55\ \mathrm{mol\ L^{-1}}$.

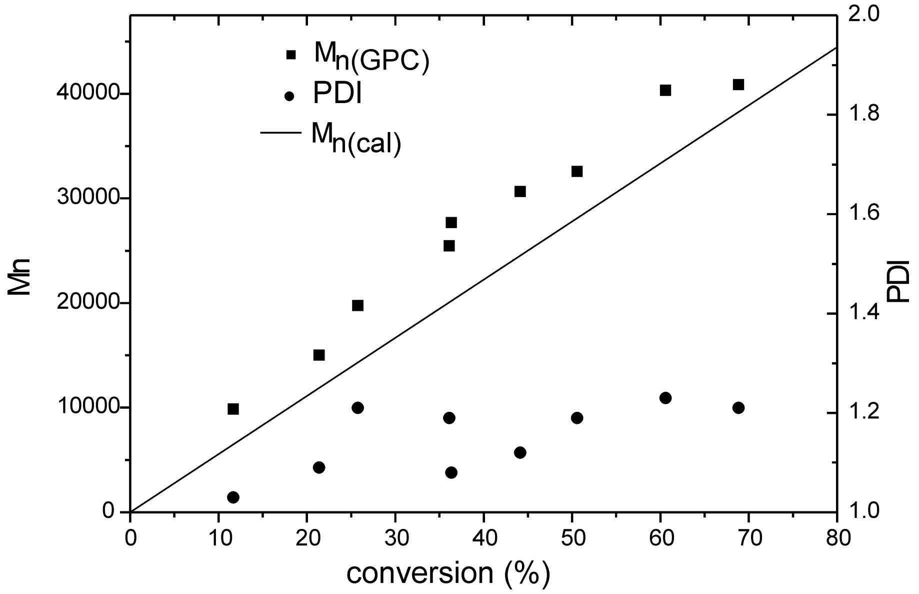


Figure 2. Relationship between M_n and conversion $[ODA]_0 : [CPDB]_0 : [AIBN]_0 = 200 : 1 : 0.5$, temperature = 60°C.

where $[m]_0$ and $[RAFT]_0$ are the starting concentrations of the monomer and the RAFT agent, x is the fractional conversion, and M_0 is the molar mass of the monomer. $M_{n,\mathrm{RAFT}}$ is the molar mass of the RAFT agent. Moreover, the molecular weight distributions PDI are demonstrated as low as 1.3 (Fig. 2).

These results indicated that the monomer ODA can be polymerized with acontrolled free-radical polymerization process with a RAFT process.

^{1}H NMR spectroscopy of the resulting PODA is shown in Fig. 3. The signals at around 1.8–2.8 ppm, 3.8–4.1 ppm (d) and 1.8–2.0 (c), 2.2–2.4 (b) are assigned to the repeat unit of ODA. The peak at around 6.7–7.5 corresponds to the protons at the phenyl group of dithioester moieties. These results indicated that ODA polymerization undergoes RAFT process in the present of CNDB at the condition mentioned above.

Obtained PODA bears dithioester terminal group, which can be used as a macro-RAFT agent to process the controlled free-radical polymerization. The polymerization of St in benzene solution with the obtained PODA as a RAFT agent was carried out at 60°C. Figure 4 shows the GPC plots of the reactant PODA and the product PODA-*b*-PSt. It shows that both the M_n and PDI change before and after the polymerization. M_n changes from 33,000 to 48,000 g mol^{-1}, which indicated that the St monomer added to the end of PODA, and PDI changes from 1.26 to 1.69. A shoulder was observed in the curve, which resulted in PDI increasing. This was the case with all the graft (cleaved) polymers prepared via the RAFT process, and the shoulder may be assignable to both the side reaction in the period of chain propagation and the dead polymers existed in the PODA.[17]

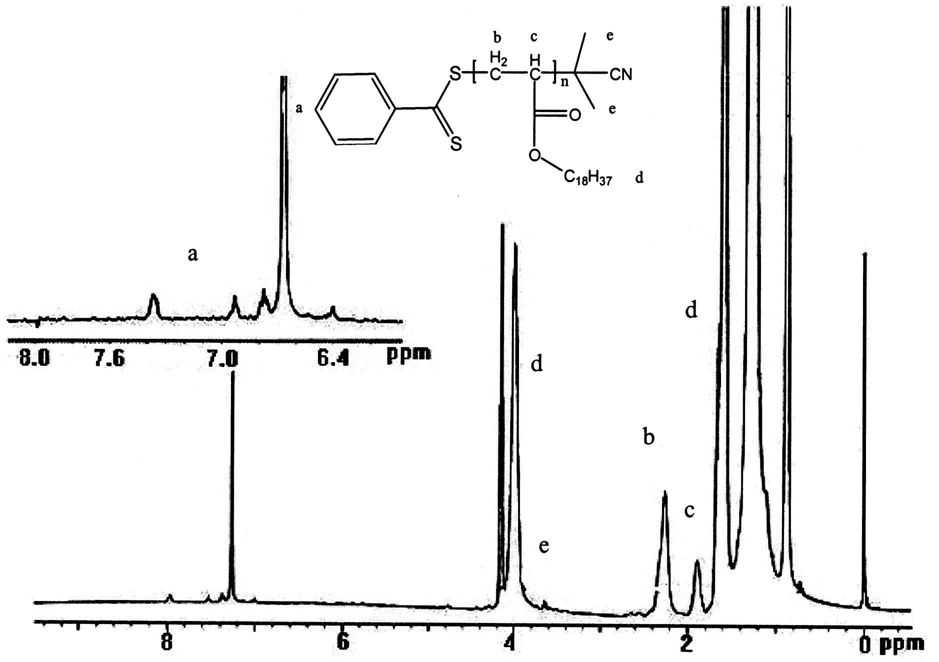


Figure 3. 400 MHz ^{1}H NMR spectroscopy of PODA obtained by RAFT polymerization in solution at 60°C. Conditions: $[ODA]_0:[CPDB]_0:[AIBN]_0 = 200:1:0.5$, $[ODA]_0 = 1.55\ \mathrm{mol\,L^{-1}}$.

Influence of $[CPDB]_0$ and $[AIBN]_0$ Ratio

According to the mechanism shown in Sch. 1, the ratio of $[CPDB]_0$ and $[AIBN]_0$ in the polymerization would have a strong effect on the resulting polymer. Therefore, a study of the polymerization of ODA at various molar ratios of $[CPDB]_0/[AIBN]_0$ was carried out at 60°C. The results are listed in Table 1.

The results showed that the PDI of obtained polymers increased and the molecular weight became unpredictable as the ratio of $[CPDB]_0/[AIBN]_0$ decreased. At lower molar ratio of $[CPDB]_0/[AIBN]_0$ (1.25 : 1 and 1 : 1) broader PDI values (1.46 and 1.54) were observed. It may caused by the insufficient chain transfer of the starting free-radicals ($P_n^{\bullet}$ in Sch. 1) as the molar ratio of $[CPDB]_0/[AIBN]_0$ decreased, the untransformed free-radicals initiated some of the polymerization and caused the conventional free-radical polymerization, thus resulting in high PDI and unpredictable molecular weight. This result indicated that in order to obtain PODA with a controlled molecular weight and low PDI, the suitable molar ratio of $[CPDB]_0/[AIBN]_0$ should be higher than 1.43 : 1.

Polymerization Temperature

The influence of polymerization temperature on the polymerization of ODA was studied; the results are shown in Figs. 5 and 6. As expected, the slope of $\ln([M_0]/[M])$ vs.

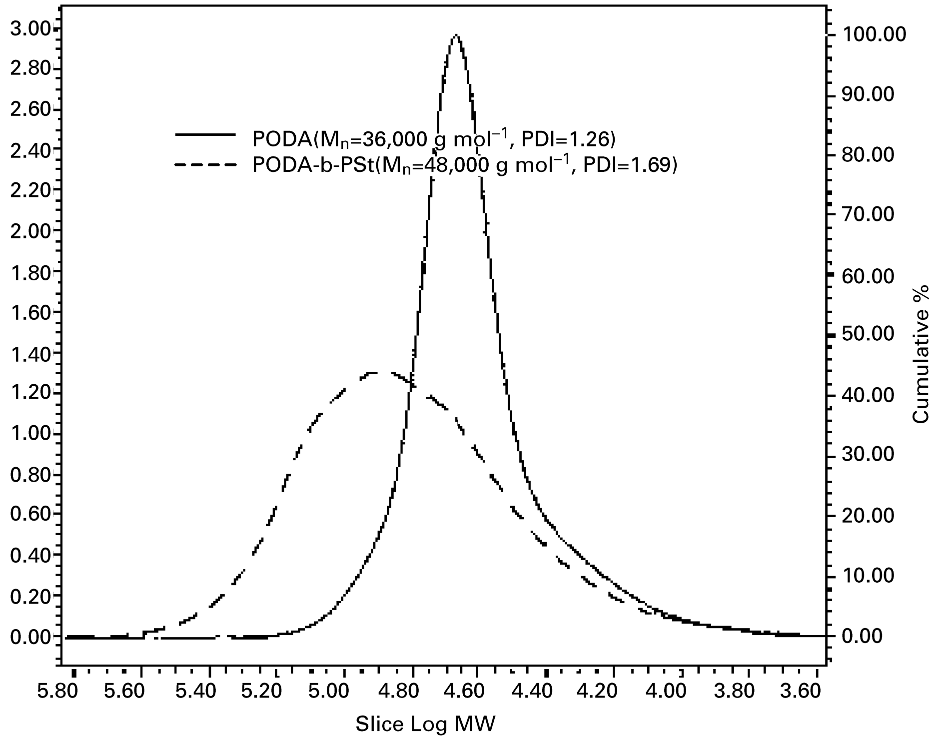


Figure 4. Gel permeation chromatography curves of PODA and PODA-*b*-PSt use PODA as macro-RAFT agent in benzene solution at 60°C with $[St]_0 : [PODA]_0 : [AIBN]_0 = 600 : 1 : 0.33$, 20 h.

reaction time increased with increasing temperature, indicating a faster rate of polymerization at a higher temperature. It is clear that some nonlinearity is exhibited in the early stages of the polymerizations. This deviation from linearity is much worse at low temperature. At lower temperatures (50°C and 60°C), there is a significant induction period, which caused by low radical flux at reduced temperatures would result in high susceptibility to impurities such as oxygen. However, it may also be caused by slow fragmentation of the dormant free-radicals formed at the start of polymerization (see Sch. 1).[8] As a result, the line does not pass the origin point. While at higher temperatures (80°C and 100°C, the fragmentation rate increases, which indicated in the results that the line passed the original point, though no induction period was found.

Moreover, the reaction temperature expresses an effect on the PDI of the resulting polymer, which is seen in Fig. 6. The number molecular weight increases proportionally to the monomer conversion at all four experimental temperatures, which indicated that the polymerization of ODA is conducted in a controlled manner. However, the polymers obtained at lower reaction temperatures (50°C and 60°C) have a smaller PDI value (lower than 1.2). As the polymerization processed at 100°C, the obtained polymer has a high PDI value (more than 1.7). This result may be caused by the possibility of primary free-radicals side reaction increasing as the temperature increased.

Table 1. Influence of molar ratio of $[CPDB]_0$ to $[AIBN]_0$ on the RAFT polymerization of ODA.

Entry	[CPDB] : [AIBN] (molar ratio)	Conversion (%)	$M_{n,\text{cal}}$	$M_{n,\text{GPC}}$	PDI
1	4.00 : 1	41.7	26,880	28,790	1.20
2	2.50 : 1	86.3	55,560	55,910	1.20
3	2.00 : 1	83.8	53,960	56,870	1.32
4	1.67 : 1	83.1	53,510	57,060	1.35
5	1.43 : 1	83.4	53,710	58,860	1.34
6	1.25 : 1	79.8	51,520	64,750	1.46
7	1.00 : 1	88.5	57,020	68,950	1.54
8	0.50 : 1	90.4	58,240	60,300	1.58
9	0.00 : 1	100	—	85,500	8.62

Note: Polymerization conditions: $[ODA]_0 : [CPDB]_0 = 200 : 1$; temperature, 60°C; Time, 20 h; $[ODA] = 1.55\,\text{mol}\,L^{-1}$.

Thermal Properties of Poly(Octadecyl Acrylate)

It is well known that poly(*n*-alkyl acrylate)s and poly(*n*-alkyl methacrylate)s with long side-chain are side-chain crystalline polymers. Extensive studies of their physical, thermal and structural properties have been reported,[24–26] but there are few reports

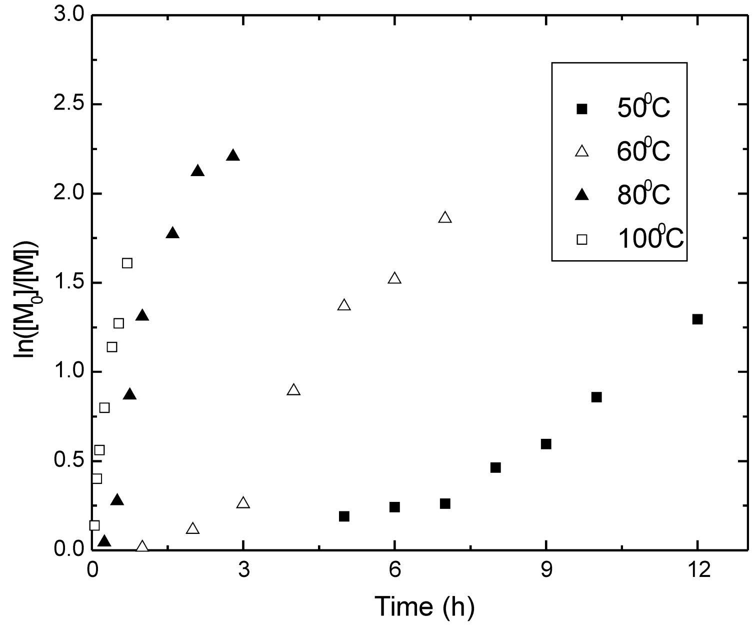


Figure 5. Plots of reaction time vs. $\ln([M_0]/[M])$ at various temperatures. $[ODA]_0 : [CPDB]_0 : [AIBN]_0 = 200 : 1 : 0.5$, $[ODA]_0 = 1.55\,\text{mol}\,L^{-1}$.

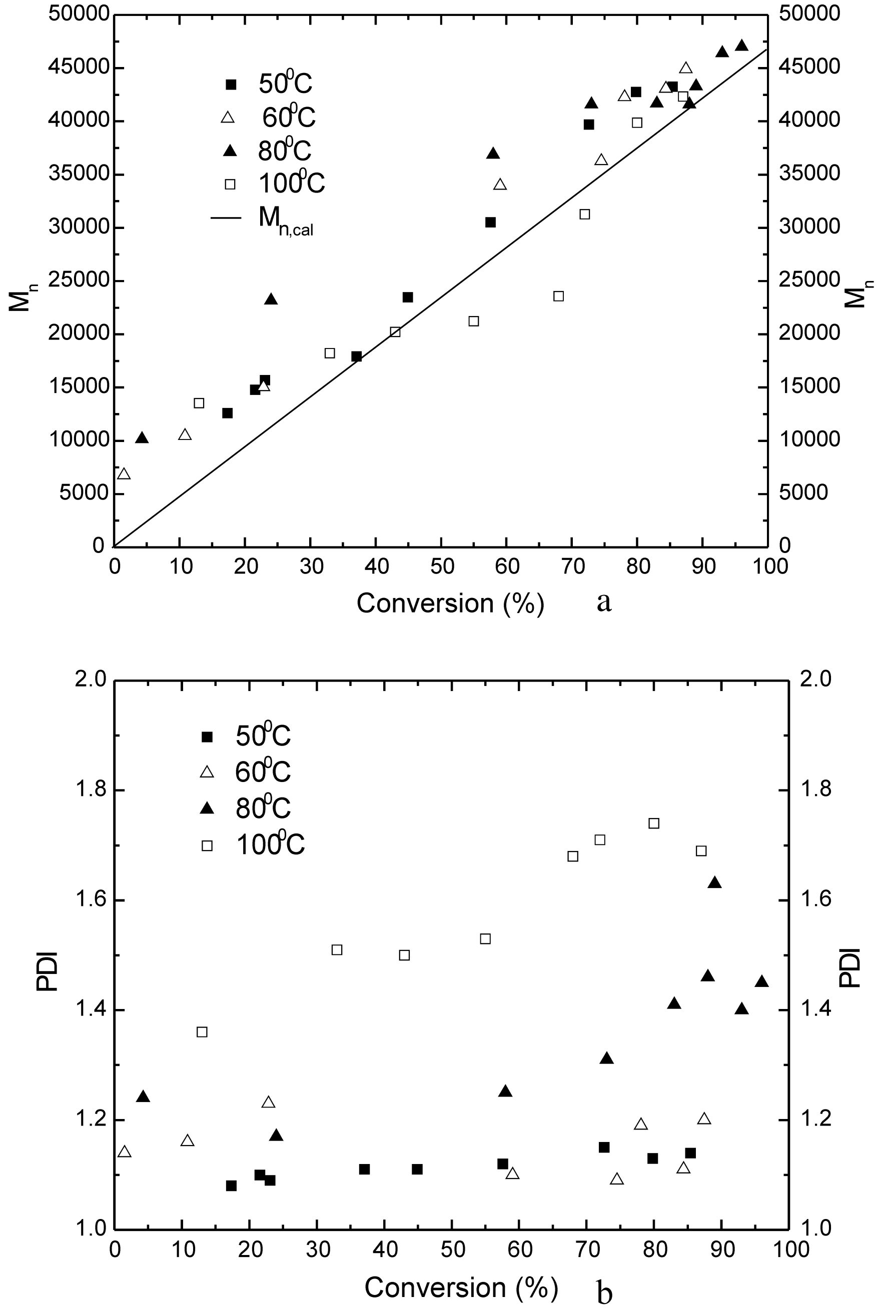


Figure 6. Plots of M_n vs. conversion (a) and PDI vs. conversion (b) at various temperatures. $[ODA]_0 : [CPDB]_0 : [AIBN]_0 = 200 : 1 : 0.5$, $[ODA]_0 = 1.55\ mol\ L^{-1}$.

concerned with the relationship between the PD and the thermal properties of these polymers.[27] In order to explore the effect of PD of the PODA on the thermal properties of the polymer, DSC measurements of PODAs, obtained by RAFT polymerization and conventional free-radical polymerization, respectively, were carried out at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. A typical thermogram is shown in Fig. 7. The melting point (T_m) and heat fusion (ΔH_m) were determined from the endothermic peaks. The thermal properties of PODA obtained by RAFT and conventional free-radical polymerization are shown in Table 2.

Table 2 shows a lower value of heat fusion (ΔH_f) or degree of crystallinity, χ_c, for the broader PD and smaller molecular weight. The polymer of entry 2 has the highest fusion heat and crystallinity. The degree of crystallinity was calculated from the following:

$$\chi_c = \frac{\Delta H_f}{\Delta H_{f0}} \tag{2}$$

where ΔH_f was measured by DSC (expressed in units or J g^{-1} of sample) and the value of ΔH_{f0} is 219.5 J g^{-1} of crystal.[29,30] 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. The thermal properties for this polymer agree well with previous published reports.[28,29]

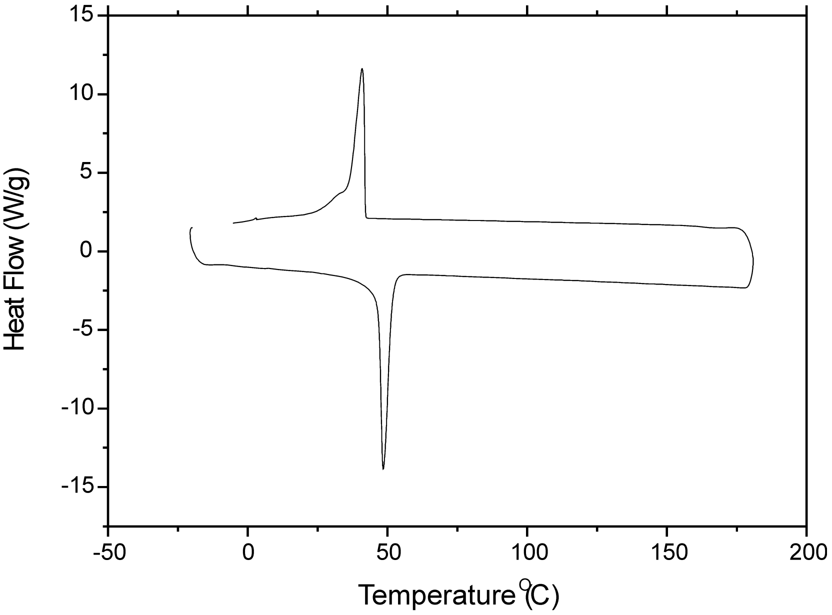


Figure 7. Typical DSC thermogram (scanning rate = 10°C min^{-1}) of PODA synthesized by RAFT polymerization at 60°C in benzene solution in the presence of AIBN as an initiator. Condition: $[\text{ODA}]_0 : [\text{CPDB}]_0 : [\text{AIBN}]_0 = 200 : 1 : 0.5$, $[\text{ODA}]_0 = 1.55\ \text{mol L}^{-1}$, $M_n = 42{,}300$, PDI = 1.15.

Table 2. Effect of different PD on the thermal and physical properties of PODA.

Entry	M_n	PDI	T_m (°C)	ΔH_f (J g^{-1})	χ_c[a]
1[b]	42,300	1.15	48.5	83.02	0.38
2[b]	14,800	1.12	47.2	104.10	0.47
3[c]	85,500	8.62	46.1	79.58	0.36

[a] The degree of crystallinity is calculated from Eq. (2).
[b] RAFT polymerization product.
[c] Conventional free-radical polymerization product.

CONCLUSION

Free-radical polymerization of ODA, using AIBN as an initiator and CPDB as a transfer agent, shows controlled free-radical characters: well controlled molecular weight, narrow molecular weight distribution, linear relationship between molecular weight and monomer conversion and first-order kinetics of the polymerization. The polymerization express controlled at the molar ratio of $[\mathrm{CPDB}]_0$ and $[\mathrm{AIBN}]_0$ is higher than 1.67 : 1, and a suitable reaction temperature is 60–80°C. DSC results show that PODA obtained from RAFT polymerization has a greater crystallinity than that polymerized by conventional polymerization.

ACKNOWLEDGMENTS

We acknowledge the financial support from the National Nature Science Foundation of China (contract No. 20176033,) and the Natural Science Foundation of Jiangsu (contact No. BK2001141).

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Received November 2002
Revised March 2003

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