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# Synthesis and characterization of poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymers using a novel macroinitiator by reversible addition-fragmentation chain transfer polymerization

**Abstract:** Synthesis of poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymers was carried out by reversible addition-fragmentation chain transfer (RAFT) polymerization of 2-vinylpyridine using a novel macroinitiator (RAFT macroinitiator). For this purpose, RAFT macroinitiator was obtained from the potassium salt of ethyl xanthogenate and poly(vinyl chloride) (PVC). Then the graft copolymers were synthesized by using RAFT macroinitiator and 2-vinylpyridine. The principal parameters such as monomer concentration, initiator concentration, and polymerization time that affect the polymerization reaction were studied. The effect of the reaction conditions on the heterogeneity index and molecular weight was also investigated. The block lengths of the graft copolymers were calculated by using  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra. The block lengths of the copolymers could be adjusted by varying the monomer and initiator concentrations. The characterizations of the samples were carried out by using  $^1\text{H}$  NMR, Fourier-transform infrared spectroscopy, gel-permeation chromatography, thermogravimetric analysis, differential scanning calorimetry, and fractional precipitation ( $\gamma$  value) techniques. RAFT polymerization is used to control the polymerization of 2-vinylpyridine over a broad range of molecular weights.

**Keywords:** block length; graft copolymer; macroinitiator; poly(vinyl chloride); reversible addition-fragmentation chain transfer (RAFT) polymerization.

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## 1 Introduction

Block or graft copolymers that provide particular combinations of physical properties are one of the most important polymeric materials used in technological applications and theoretical research because of their superior properties based on microphase separation (1–21). Graft copolymers are branched copolymers in which the side chains are different from the main chain. By using functional polymers containing appropriate alkyl halide groups along the backbone as a macroinitiator, graft copolymers with a controlled structure can be obtained (22). The well-defined synthesis of graft copolymers is an important topic in macromolecular chemistry (23). Macrointermediates such as macroinitiators, macromonomers, and macro-crosslinkers have been extensively used for designing various block or graft copolymers via a radical initiated process (24–36).

Polymers of a well-defined structure and molecular weight can be synthesized by controlled radical-polymerization methods, such as nitroxide-mediated polymerization (37, 38), atom-transfer radical polymerization (25, 39–44), and reversible addition-fragmentation chain transfer (RAFT) polymerization (33, 45–60). RAFT polymerization is one of the most recently developed controlled radical-polymerization methods and is an important technique for the synthesis of copolymers. The versatility of the method is shown by its compatibility with many monomers and reaction conditions. Reversible chain transfer includes homolytic substitution, addition fragmentation, or some other transfer mechanisms (45–56).

In earlier studies, we reported the synthesis of a new dual macromonomer initiator obtained from the potassium salt of ethyl xanthogenate and terminally brominated poly(ethylene glycol) for RAFT polymerization, which is a method of controlled/“living” polymerization

(33, 58). In this study, we report the synthesis of a novel macroinitiator (RAFT macroinitiator) obtained from the potassium salt of ethyl xanthogenate and poly(vinyl chloride) (PVC) for RAFT polymerization, which is a method of controlled/living polymerization. Poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymers were synthesized using RAFT macroinitiator by RAFT polymerization of the reactants. Graft copolymerization was studied by changing some polymerization conditions such as monomer concentration, initiator concentration, and polymerization time. The synthesized graft copolymers could be used to prepare copolymers with the desired segment ratio by changing the polymerization conditions.

## 2 Materials and methods

### 2.1 Materials

The potassium salt of ethyl xanthogenate, tetrahydrofuran (THF), 2-vinylpyridine, and methanol were supplied by Merck (Merck KGaA, Germany) and used as received. 2,2'-Azobisisobutyronitrile (AIBN), *N,N*-dimethylformamide (DMF), and chloroform were obtained from Sigma-Aldrich (Sigma-Aldrich Co., USA) and used as received. Diethyl ether and petroleum ether were supplied from Carlo Erba A.G. (Carlo Erba Reagents, Italy) and used as received. All other chemicals were reagent grade and used as supplied.

### 2.2 Instrumentation

The molecular weights and heterogeneity indexes were measured with a Polymer Labs PL-GPC 220 (Polymer Laboratories Ltd., UK) gel-permeation chromatography (GPC) instrument with THF as the solvent. A calibration curve was obtained with four polystyrene standards: 2960, 50,400, and 696,500 Da, of low polydispersity. Fourier-transform infrared (FTIR) spectra were recorded using a Nicolet-520 model FTIR spectrometer. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectra of the samples in dimethyl sulfoxide and CDCl<sub>3</sub> as the solvent, with tetramethylsilane as the internal standard, were recorded using a Bruker Ultra Shield Plus, ultra long hold time 400 MHz NMR spectrometer (Bruker Corporation, Germany). Thermal analysis measurements of the samples were carried out under nitrogen using a Perkin-Elmer Pyris 1 TGA and a Spectrum thermal analyzer (PerkinElmer Inc., USA) to determine thermal degradation. Differential scanning calorimetry (DSC) measurement was carried out by using

a Perkin-Elmer DSC 8000 series thermal analysis system (PerkinElmer Inc., USA). Dried sample was heated at a rate of 10°C/min under nitrogen atmosphere.

### 2.3 Synthesis of a novel macroinitiator

PVC was purified as follows: It was dissolved in THF, precipitated in methanol, and dried under vacuum at 45°C for 24 h before use. Purified PVC [4.50 g (6.82×10<sup>-3</sup> mol/l)] was reacted with 11.60 g (2.42 mol/l) of the potassium salt of ethyl xanthogenate in 30 ml of THF at 25°C for 48 h. The solution was filtered to remove the unreacted xanthate, and the solvent was removed by a rotary evaporator. RAFT macroinitiator was precipitated in cold diethyl ether/petroleum ether (1:1) solution and dried under vacuum at room temperature for 4 days.

### 2.4 RAFT polymerization of 2-vinylpyridine by using the macroinitiator

Specified amounts of RAFT macroinitiator, 2-vinylpyridine, AIBN, and DMF (as solvent) were charged separately into a Pyrex tube, and subsequently, argon was purged into the tube through a needle. The tube was tightly capped with a rubber septum and was dropped into an oil bath thermostated at 90°C. After the polymerization, the reaction mixture was poured into an excess of methanol to separate poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymers. The graft copolymers were dried at 40°C under vacuum for 4 days. The yield of the graft copolymer was determined gravimetrically.

### 2.5 Fractional precipitations of the polymers

Fractional precipitations of the polymers were carried out according to the procedure reported in the literature (43, 61). Vacuum-dried graft copolymer sample (approximately 0.5 g) was dissolved in 5 ml of THF. Petroleum ether was added dropwise to the polymer solution with stirring until turbidity occurred. At this point, 1–2 ml of petroleum ether was added to complete the precipitation. The precipitate was removed by filtration. The solvent was THF and the nonsolvent was petroleum ether. In this solvent-nonsolvent system, the  $\gamma$  value was calculated as the ratio of the total volume of nonsolvent used for the first fraction to the volume of solvent used.

$$\gamma \text{ value} = \frac{\text{Volume of nonsolvent (ml, petroleum ether)}}{\text{Volume of solvent (ml, THF)}}$$

The nonsolvent addition into the filtrate solution was continued according to the same procedure mentioned above to determine the  $\gamma$  value for the second fraction if there was one.

## 2.6 Measurement of swelling ratio in distilled water

Measurement of the swelling ratios ( $q_v$ ) of the graft copolymers (62) was carried out by storing 0.4 g of the samples in 30 ml of distilled water for 48 h at 20°C. The  $q_v$  of the graft copolymer was calculated by the following equations:

$$A = \frac{\text{Swollen copolymer (g)} - \text{Dry copolymer (g)}}{\text{Dry copolymer (g)}}$$

$$q_v = 1 + \frac{A}{d_{\text{water}}}$$

The density of distilled water ( $d_{\text{water}}$ ) is taken as 1 g/ml.

## 3 Results and discussion

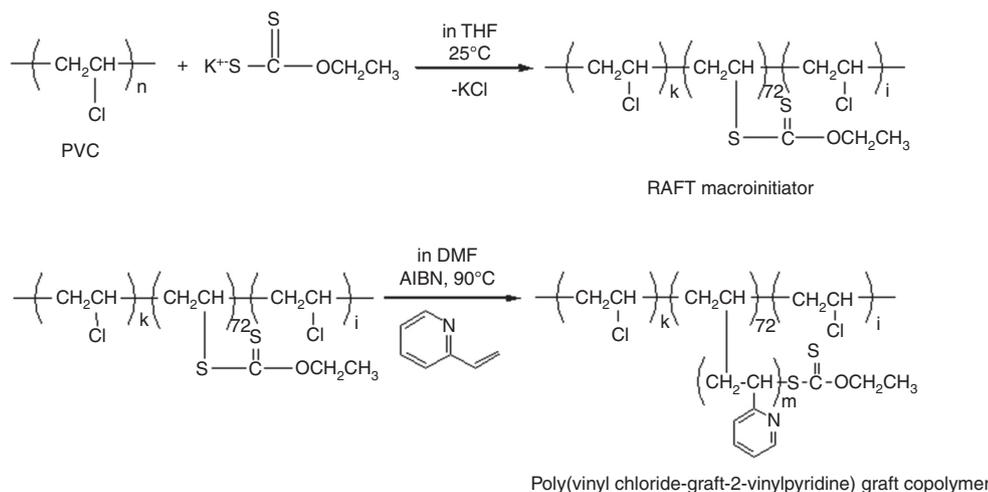
### 3.1 Synthesis of RAFT macroinitiator

The goal of this work was to synthesize a novel macroinitiator and to evaluate graft copolymerization with 2-vinylpyridine by RAFT method in view of the effect of some different polymerization conditions. RAFT macroinitiator was synthesized by the reaction of the potassium salt of ethyl xanthogenate with PVC. The product yield was approximately 36 wt%. The basic outline for the

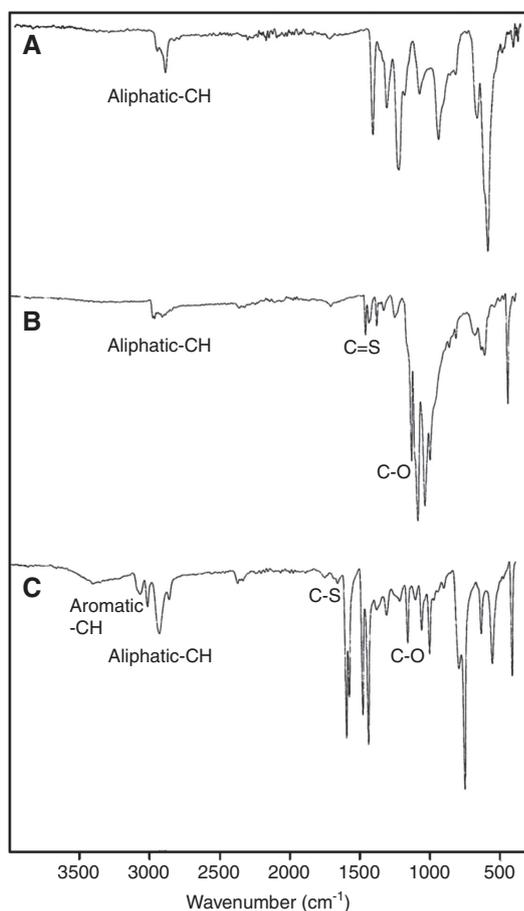
synthesis of RAFT macroinitiator is shown in Scheme 1. The FTIR spectrum of PVC in Figure 1A shows the signals at 2910 and 2967  $\text{cm}^{-1}$  for aliphatic -CH and -CH<sub>2</sub> groups. The FTIR spectrum of RAFT macroinitiator in Figure 1B shows the signals at 2981, 2968, and 2951  $\text{cm}^{-1}$  for aliphatic -CH, -CH<sub>2</sub>, and -CH<sub>3</sub> groups, respectively, 1462  $\text{cm}^{-1}$  for -C=S groups, and 1138  $\text{cm}^{-1}$  for -C-O groups. The <sup>1</sup>H NMR spectrum of PVC in Figure 2A shows the signals at 2.2 ppm for -CH<sub>2</sub> protons and 4.4 ppm for -CHCl protons. The <sup>1</sup>H NMR spectrum of RAFT macroinitiator in Figure 2B shows the signals at 1.2 ppm for -CH<sub>3</sub> protons, 2.2 ppm for -CH<sub>2</sub> protons, 3.1 ppm for -SCH protons, and 4.4 ppm for -OCH<sub>2</sub> and -CHCl protons. The numbers of the xanthogenate groups of RAFT macroinitiator were calculated using the integral ratios of the signals corresponding to the -CH<sub>3</sub> protons of ethyl xanthogenate group ( $\delta=1.2$  ppm), and the -CH<sub>2</sub> groups of the PVC group ( $\delta=2.2$  ppm) in the <sup>1</sup>H NMR spectrum of the macroinitiator. There were approximately 72 xanthogenate groups per chain.

### 3.2 Synthesis of poly(vinyl chloride-graft-2-vinylpyridine) graft copolymers by RAFT polymerization

The RAFT polymerization of 2-vinylpyridine initiated by RAFT macroinitiator is shown in Scheme 1. This process creates new active sites on the thiocarbonate groups for RAFT polymerization. The FTIR spectrum of poly(vinyl chloride-graft-2-vinylpyridine) graft copolymer (PD-4) in Figure 1B shows the signals at 3055  $\text{cm}^{-1}$  for aromatic -CH groups; 3004, 2921, and 2850  $\text{cm}^{-1}$  for aliphatic -CH, -CH<sub>2</sub>, and -CH<sub>3</sub> groups, respectively; 1646  $\text{cm}^{-1}$  for -C=S groups; and 1147  $\text{cm}^{-1}$  for -C-O groups. The <sup>1</sup>H NMR spectrum of the



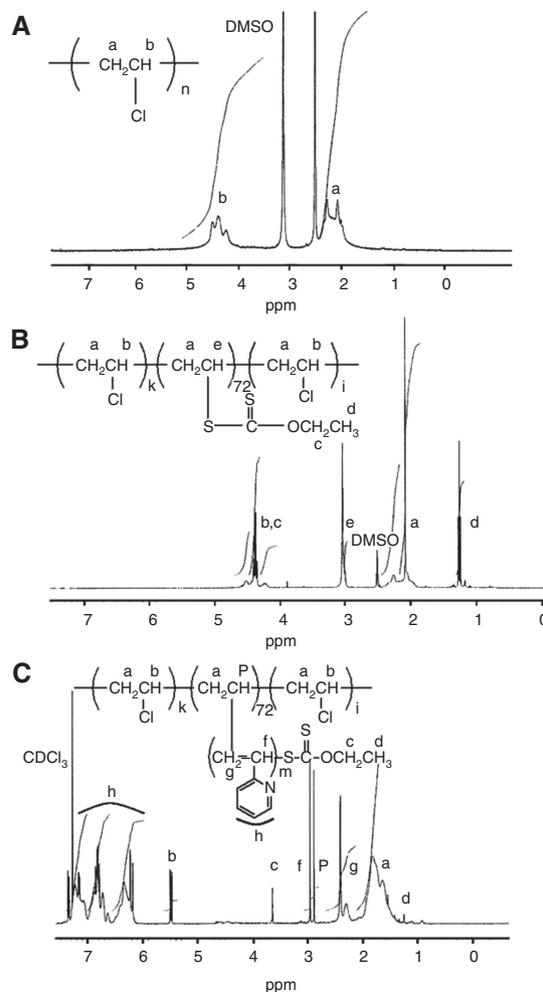
**Scheme 1** Reaction pathways in the synthesis of poly(vinyl chloride-graft-2-vinylpyridine) graft copolymer.



**Figure 1** FTIR spectra of PVC (A), RAFT macroinitiator (B), and poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymer (PD-4 in Table 1) (C).

graft copolymer (PD-4) in Figure 2C shows the signals at 1.2 ppm for  $-\text{CH}_3$  protons of the ethyl xanthogenate group, 1.8 ppm for  $-\text{CH}_2$  protons of the PVC group, 2.4 ppm for  $-\text{CH}_2$  protons of the poly(2-vinylpyridine) group, 2.9 ppm for  $-\text{CH}$  protons of PVC-attached poly(2-vinylpyridine) group, 3.0 ppm for  $-\text{CH}$  protons of the poly(2-vinylpyridine) group, 4.7 ppm for  $-\text{OCH}_2$  protons of the ethyl xanthogenate group, 5.5 ppm for  $-\text{CHCl}$  protons of the PVC group, and 6.3, 6.9, and 7.2 ppm for aromatic  $-\text{CH}$  protons of the poly(2-vinylpyridine) group.

The effects of polymerization time, initiator concentration, and monomer concentration on the copolymerization in the presence of RAFT macroinitiator by the application of RAFT processes were studied (Table 1). The monomer conversion was calculated from the weight of recovered graft copolymer. The conversion of monomer was between 48.97 and 67.35 wt%. High conversion of 2-vinylpyridine is obtained by the graft polymerization of 2-vinylpyridine initiated with RAFT macroinitiator. For polymerizations of longer durations, polymers of higher molecular weights are



**Figure 2**  $^1\text{H}$  NMR spectra of PVC (A), RAFT macroinitiator (B), and poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymer (PD-4 in Table 1) (C).

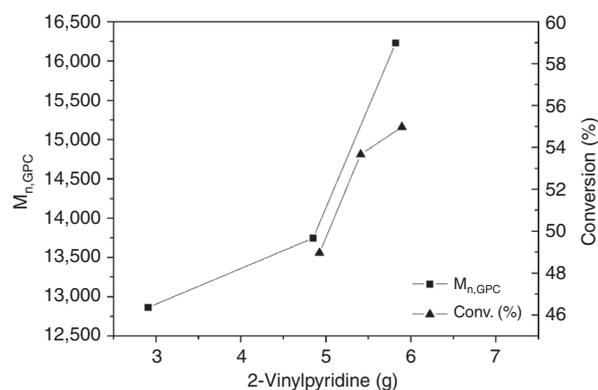
obtained. Longer polymerization time causes higher copolymer yields; these results are in good agreement with those stated by Heidenreich and Puskas (63) for RAFT polymerization. Higher amounts of RAFT macroinitiator cause a higher graft copolymer yield. Interestingly, the value of  $M_n$  can only decrease if new chains are generated, which, however, is not in accordance with a controlled polymerization. Increased amounts of initiator in the reaction mixture lead to the formation of a higher number of active centers. Consequently, increased numbers of growing macroradicals are formed in the system. Hence, it may be expected that they have shorter poly(2-vinylpyridine) segments, which is confirmed by a decrease in the molecular weights of the graft copolymers, as shown in Table 1. The same situation was also observed in our previous articles (58–60). Increasing the amount of monomers also generally causes an increase in both the yield and the molecular weights of the copolymers as expected. However, the molecular

**Table 1** The effects of polymerization time, amount of RAFT macroinitiator, and amount of the monomer on the graft copolymerization.

Code	RAFT macroinitiator		2-Vinylpyridine		Time (min)	Yield (g)	Conversion (wt%)	$\gamma^a$	$q_v$ (in distilled water)	$M_{n,GPC}$	$M_w/M_n$	PVC/poly(2-vinylpyridine) segment (mol/mol)
	g	mol/l	g	mol/l								
PD-4	0.204	$1.81 \times 10^{-3}$	3.880	9.238	130	2.431	59.52	2.00	1.50	12,570	1.89	1.00/0.83
PD-5	0.200	$1.78 \times 10^{-3}$	3.880	9.238	200	2.748	67.35	2.06	1.42	15,004	1.84	-/-
PE-2	0.203	$1.80 \times 10^{-3}$	2.910	6.929	70	1.855	59.59	1.80	1.72	12,863	2.42	1.00/0.83
PE-3	0.202	$1.79 \times 10^{-3}$	4.850	11.547	70	2.474	48.97	2.06	1.88	13,746	1.75	1.00/0.84
PE-4	0.203	$1.80 \times 10^{-3}$	5.820	13.857	70	3.232	53.67	2.08	1.28	16,229	1.66	1.00/0.86
PE-5	0.202	$1.79 \times 10^{-3}$	6.790	16.167	70	3.844	54.98	2.06	1.57	16,063	1.80	1.00/0.85
PG-4	0.250	$2.22 \times 10^{-3}$	3.880	9.238	70	2.255	54.60	2.06	1.33	23,459	1.22	1.00/0.85
PG-5	0.350	$3.11 \times 10^{-3}$	3.880	9.238	70	2.415	57.09	2.00	1.40	17,529	1.97	1.00/0.79

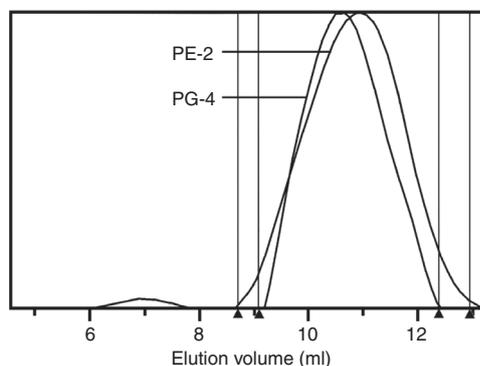
Polymer temperature=90°C. <sup>a</sup>Nonsolvent (petroleum ether, ml)/solvent (THF, ml); AIBN, 0.022 g; DMF, 4 ml.

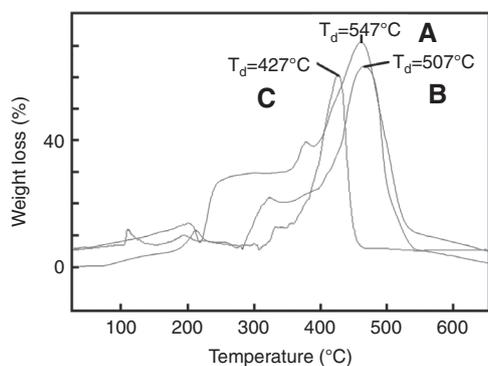
weight decreases for PE-5 in comparison to PE-4 (Table 1) with increase in the monomer concentration reacted at the same temperature. At higher amounts of monomer, a deviation from normal behavior was observed. This situation could be attributed to the increase in viscosity of the polymerization medium as shown in our previous articles (24, 60). Dependence of 2-vinylpyridine concentration on  $M_n$  for the copolymerization is shown in Figure 3. The  $M_w/M_n$  values of the poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymers are between 1.22 and 2.42 (Table 1). Because of the use of a macroinitiator including PVC,  $M_w/M_n$  values of the graft copolymers are relatively higher than expected. All GPC chromatograms were unimodal. The GPC chromatograms of the copolymers (PE-2 and PG-4) are shown in Figure 4. A significant GPC trace was observed at lower elution volume in Figure 4. The GPC trace showed low yields and high molar weights of products, which were not obtained appreciably. The  $q_v$  values of the graft copolymers in distilled water varied from 1.28 to 1.88, which can be attributed to low water absorbance of the copolymers.

**Figure 3** Dependence of 2-vinylpyridine on  $M_n$  for poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymers.

The polymer composition of the graft copolymers was calculated using the integral ratios of the signals corresponding to the  $-CH_2$  groups of PVC ( $\delta=1.7-1.8$  ppm) and the aromatic  $-CH$  of poly(2-vinylpyridine) ( $\delta=6.2-8.4$  ppm). In general, PVC segments of the graft copolymers are more than the poly(2-vinylpyridine) segments of the copolymers. Generally, as the monomer feed increased, the poly(2-vinylpyridine) content increased at the copolymers (Table 1). The poly(2-vinylpyridine) content increased with increasing initiator feed at the copolymerization as shown in Table 1. These results indicate that RAFT polymerization can be used to prepare graft copolymers containing the desired segment ratio by changing the polymerization conditions.

Thermogravimetric analysis (TGA) showed interesting properties of the graft copolymers indicating continuous weight loss starting from nearly 95°C to nearly 480°C with a derivative at 427°C (PD-5) as shown in Figure 5. The first decomposition observed at 111°C may have been caused by the solvent traces. The  $T_g$  value of the graft copolymer (PD-4) was 140°C (Figure 6). The  $T_g$  values reported in the

**Figure 4** GPC profiles of the graft copolymers (PE-2 and PG-4 in Table 1) with elution volume.



**Figure 5** TGA curves of PVC (A), RAFT macroinitiator (B), and poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymer (PD-5 in Table 1).

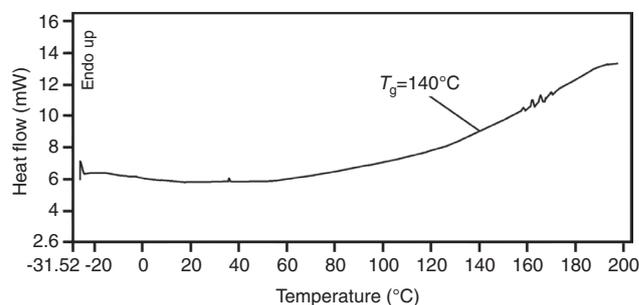
literature for homo poly(2-vinylpyridine) and homo PVC were 95°C (64) and 80°C (65), respectively. The  $T_g$  value of the graft copolymer changed to a value that was more than the values of homo PVC and homo poly(2-vinylpyridine). Only one glass transition was detected. It could be concluded that the corresponding homopolymers were relatively mixtures. This can be attributed to the high miscibility of the polymerizable 2-vinylpyridine groups of the graft copolymer and PVC moieties of RAFT macroinitiator. The same situation (the observation of only one glass transition) can also be seen in our previous articles (25, 43, 60).

### 3.3 Fractional precipitation

The  $\gamma$  values of poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymers were between 1.80 and 2.08, as shown in Table 1. In the solvent-nonsolvent system, the  $\gamma$  values were found to be 1.10–1.22 for homo PVC and 0.40–0.44 for homo poly(2-vinylpyridine). The  $\gamma$  values of the graft copolymers were different from those of homo PVC and homo poly(2-vinylpyridine). Fractional precipitation behavior provides an evidence for the formation of graft copolymer.

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**Figure 6** DSC curve of poly(vinyl chloride-*graft*-2-vinylpyridine) graft copolymer (PD-4 in Table 1).

## 4 Conclusions

RAFT macroinitiator containing PVC has demonstrated the characteristic macroinitiator behavior in the graft copolymerization of 2-vinylpyridine by RAFT polymerization. The graft copolymers are obtained in relatively high yield and molar weight. The proposed procedure for the preparation of graft copolymers is simple and efficient. The block length can be regulated by varying the monomer and initiator concentrations. Basically, by controlling the polymerization parameters such as the macroinitiator concentration, monomer concentration, and polymerization time, RAFT macroinitiators can be promising materials in order to obtain graft copolymers.

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