

SYNTHESIS OF GRAFT COPOLYMERS WITH POLYISOBUTYLENE BRANCH CHAINS*

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Abstract The copolymerization of 4-vinylbenzyl chloride (VBC) and vinyl acetate (VAC) was carried out in toluene at 75°C *via* radical polymerization using 2,2'-azo-bis-(isobutyronitrile) (AIBN) as an initiator. The random copolymers of poly(4-vinylbenzyl chloride-*co*-vinyl acetate) (P(VBC-*co*-VAC)) with number average molecular weight (M_n) from 2000 to 6900, relatively narrow molecular weight distribution (MWD, M_w/M_n *ca.* 2.0) and with different copolymer composition of 4-vinylbenzyl chloride (VBC) from 17 mol% to 62 mol% could be obtained. The P(VBC-*co*-VAC) copolymers with an average number of 7 to 13 initiating sites of benzyl chloride per macromolecule could be used for the cationic polymerization of isobutylene (IB). The cationic polymerizations of IB were further conducted by using P(VBC-*co*-VAC) copolymers as macroinitiators in conjunction with $TiCl_4$ at -40°C in CH_2Cl_2 . The effects of VBC/ $TiCl_4$ (molar ratio) on monomer conversion, M_n and MWD of the resultant copolymers were investigated under 3 sets of conditions. It is found that P(VBC-*co*-VAC)-*g*-PIB copolymers with relatively narrow MWD (M_w/M_n *ca.* 2.0) and with terminal *tert*-chlorine functional groups in branched PIB chains could be successfully synthesized when VBC/ $TiCl_4$ (molar ratio) was set in the range from 0.10 to 1.12. The unimodal GPC curve of the P(VBC-*co*-VAC)-*g*-PIB copolymers by RI detector was almost in harmony with the GPC curve by UV detector. The TEM image of the P(VBC-*co*-VAC)-*g*-PIB copolymer stained by RuO indicated that the copolymer formed a two-phase morphology with P(VBC-*co*-VAC)-rich domains of 20–100 nm in size tethered by PIB branch segments.

Keywords: Isobutylene; Cationic polymerization; Macroinitiator; Graft copolymerization.

INTRODUCTION

Graft copolymers have been developing for their particular macromolecular architecture and morphology in many applications, such as in surface functionalization, chemical modification, DNA delivery *etc*^[1–7]. The synthesis of graft copolymers can be conducted *via* different routes, *e.g.* “grafting from”^[7–9], “grafting onto”^[1, 10] or “macromonomer”^[11–13]. The graft copolymerization from a macroinitiator chain with side functional groups is one of the most efficient methods for macromolecular engineering. The macroinitiators with benzyl chloride initiating functional group can be synthesized by common or controlled free radical polymerization^[8, 9, 14–21]. 4-Chloromethylstyrene (VBC) is a commercially available comonomer for synthesis of copolymers with side active benzyl chloride functions along the copolymer chains. These copolymers with VBC structural units could be used as macroinitiators to provide active sites for initiating cationic polymerization. The macroinitiator, consisting of poly(methyl methacrylate)-*b*-poly[styrene-*co*-(4-chloromethylstyrene)] could be used for cationic polymerization of isobutylene yielding graft copolymers^[15–16]. In our previous publications^[22–24], the graft

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polymerization of isobutylene from the macroinitiators with different functional active initiating sites, such as poly(vinyl acetate) and poly(vinyl acetate-*co*-isopropenyl acetate), had been conducted and the graft copolymers with branched polyisobutylene chains could be obtained. Therefore, in this paper, we investigated the synthesis and characterization of copolymers *via* graft polymerization of isobutylene from a novel macroinitiator consisting of poly(4-vinylbenzyl chloride-*co*-vinyl acetate).

EXPERIMENTAL

Materials

Vinyl acetate (VAC, 99%, Beijing Chemical Reagents Company) was distilled under vacuum before use. 2,2'-Azo-bis-(isobutyronitrile) (AIBN) was recrystallized from methanol and dried in vacuum. Titanium tetrachloride (TiCl₄, 99%, Beijing Yili Fine Chemical Co. Ltd) was used without further purification. 2,6-Di-*tert*-butyl peroxide (DtBP, 97%, Acros), dichloromethane (CH₂Cl₂) and *n*-hexane (Hex) were dried over calcium hydride (CaH₂) and distilled before use. 4-Vinylbenzyl chloride (VBC, 90%, Acros Corp.), isobutylene (IB, 99.9%, Beijing Yanshan Petroleum Chemical Company), toluene (99.5%, Beijing Chemical Co.), petroleum ether (99%, Beijing Chemical Co.) and tetrahydrofuran (THF, 99%, Beijing Yili Fine Chemical Co. Ltd) were used as received.

Polymerization

Synthesis of macroinitiator poly(4-vinylbenzyl chloride-co-vinyl acetate)

A typical procedure is described as follows (CV₁): 55 mL of VAC, 0.615 g of AIBN and 43 mL of toluene were added to a 250 mL 3-necked round-bottomed flask. Oxygen was removed by flushing with dry nitrogen for more than 5 min, then 1.7 mL of 4-vinylbenzyl chloride was added by a syringe. The copolymerization was carried out at 75°C for 9 h. The resulting polymer was precipitated in petroleum ether (30–60°C) and then further purified by dissolution and precipitation for 3 times. Finally, the poly(4-vinylbenzyl chloride-*co*-vinyl acetate) copolymer (P(VBC-*co*-VAC)) was dried at 40°C under vacuum.

Synthesis of graft copolymer P(VBC-co-VAC)-g-PIB

The above copolymer P(VBC-*co*-VAC) was used as a macroinitiator for cationic polymerization of IB. A typical procedure is described as follows: 0.100 g of P(VBC-*co*-VAC) was dissolved in 2.0 mL of CH₂Cl₂ to prepare the solution. 21.8 mL of CH₂Cl₂, 2.0 mL of the above macroinitiator solution, 1.2 mL TiCl₄ solution in CH₂Cl₂ ([TiCl₄] = 1.0 mol/L) and 5.0 mL of IB solution in CH₂Cl₂ ([IB] = 4.0 mol/L) were added to a glass reactor under a dry nitrogen atmosphere to conduct the polymerization reaction at –40°C. The polymerization was quenched with pre-chilled ethanol after 30 min. The quenched reaction mixtures were diluted with *n*-hexane and then washed with water to remove the co-initiator residues until neutral. The graft copolymers were purified by extracting macroinitiator P(VBC-*co*-VAC) with butanone.

Characterization

The monomer conversion was measured gravimetrically.

Determinations of number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of the resulting polymers were performed by gel permeation chromatography (GPC, Waters 515–2410) with three Styragel GPC columns (HT3, HT5, HT6E) and both RI and UV detectors. THF was used as solvents with a flow rate of 1 mL/min. Polystyrene standards were used for calibration. The UV trace corresponded to the phenyl group at 258 nm.

The microstructure and composition of copolymers of P(VBC-*co*-VAC) and P(VBC-*co*-VAC)-g-PIB were characterized by ¹H-NMR. The ¹H-NMR spectra were acquired on a Bruker AV600 MHz spectrometer in CDCl₃ at 25°C with tetramethylsilane (TMS) as internal standard. The copolymer compositions, expressed by VBC% mol in P(VBC-*co*-VAC), were determined according to following equation:

$$\text{VBC (mol\%)} = \frac{\frac{1}{2}A_{4.55}}{\frac{1}{2}A_{4.55} + A_{4.85}} \times 100\% \quad (1)$$

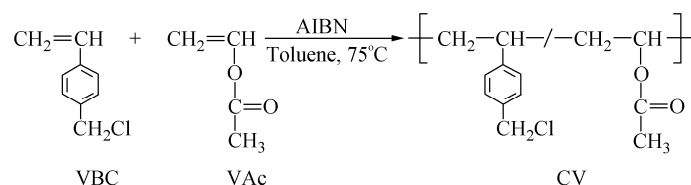
where, $A_{4.55}$ is the integral value at $\delta = 4.55$ assigned to $-\text{CH}_2\text{Cl}$ in VBC structural units; $A_{4.85}$ is the integral value at $\delta = 4.85$ assigned to $-\text{CH}-$ in VAC structural units.

The morphology of P(VBC-*co*-VAC)-*g*-PIB graft copolymers was characterized by using a transmission electron microscope (TEM, Hitachi H-800) at 150 kV. The P(VBC-*co*-VAC)-*g*-PIB graft copolymers in toluene (2 mg/mL) was used to form copolymer films on 3 mm copper grids and stained by ruthenium tetroxide (RuO_4).

RESULTS AND DISCUSSION

Synthesis of Macroinitiator P(VBC-*co*-VAC)

The copolymerization of 4-vinylbenzyl chloride (VBC) and vinyl acetate (VAC) initiated by 2,2'-azo-bis-(isobutyronitrile) (AIBN) was conducted in toluene at 75°C as described in Scheme 1. The experimental details and results are summarized in Table 1.



Scheme 1 Synthesis of copolymer P(VBC-*co*-VAC) of VBC and VAC

Table 1. Synthesis of macroinitiators (CV): experimental details and results

Macroinitiator	[VBC] (mol/L)	[VAc] (mol/L)	[AIBN] (mol/L)	Yield (%)	M_n	M_w/M_n	VBC (mol%)	Average number of initiating sites per copolymer chain
CV ₁	0.14	10.6	0.026	12	6400	2.0	17	11
CV ₂	0.11	5.95	0.038	12	2900	2.1	26	7
CV ₃	0.14	3.03	0.010	3	2800	1.3	55	13
CV ₄	0.45	8.01	0.160	17	2000	1.8	62	10

CV: P(VBC-*co*-VAC)

It can be seen from Table 1 that the 4 kinds of P(VBC-*co*-VAC) with different copolymer composition of VBC from 17 mol% to 62 mol% could be prepared. The number average molecular weight of P(VBC-*co*-VAC) decreased from 6400 to 2000 with increasing VBC content from 17 mol% to 62 mol%. The representative GPC traces recorded by simultaneous RI and UV ($\lambda = 258$ nm) detectors for CV₂ copolymer are given in Fig. 1. The GPC curve recorded by UV detector which is only sensitive to VBC units, is consistent with the GPC curve recorded by RI detector, which is sensitive to both VAC and VBC units. It can be observed that the corresponding unimodal GPC curves by dual RI and UV detectors almost coincide with each other. This result indicated that the VBC units distributed along the P(VBC-*co*-VAC) copolymer chains. Thus, the P(VBC-*co*-VAC) copolymers with an average number of 7 to 13 active sites of benzyl chloride functional groups per macromolecular chain could be used for initiating the cationic polymerization of isobutylene.

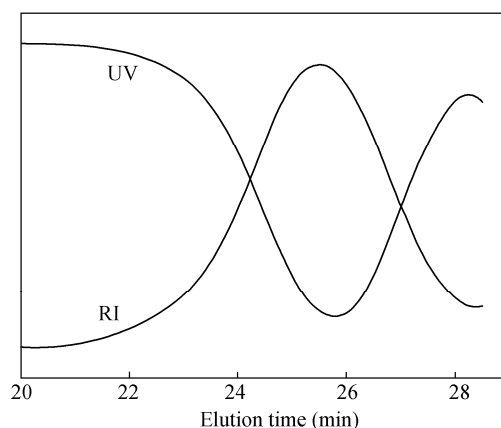


Fig. 1 GPC/UV traces of macroinitiator P(VBC-co-VAC) (CV_2 : $M_n=2900$, $M_w/M_n=2.1$)

The microstructure and composition of P(VBC-co-VAC) copolymers were analyzed by $^1\text{H-NMR}$. The representative $^1\text{H-NMR}$ spectrum is shown in Fig. 2. The signal (b) at $\delta=1.72$ is assigned to the methine proton connected with benzene ring, and signal (e) at $\delta=4.55$ is assigned to protons of chloromethyl ($-\text{CH}_2\text{Cl}$) group in VBC units. The observed signals at $\delta=7.19$ and 6.18 reflect phenyl groups in VBC units. The signal (g) at $\delta=2.03$ is assigned to methyl ($-\text{CH}_3$) group connected with carbonyl ($-\text{CO}-$), and signal (f) at $\delta=4.85$ is assigned to the methine proton connected with ester group in VAC units. It indicates that there existed VAC and VBC structural units in the copolymer P(VBC-co-VAC) products.

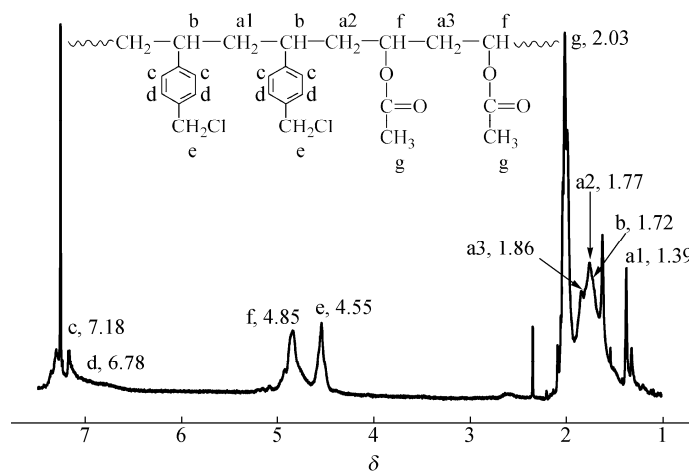


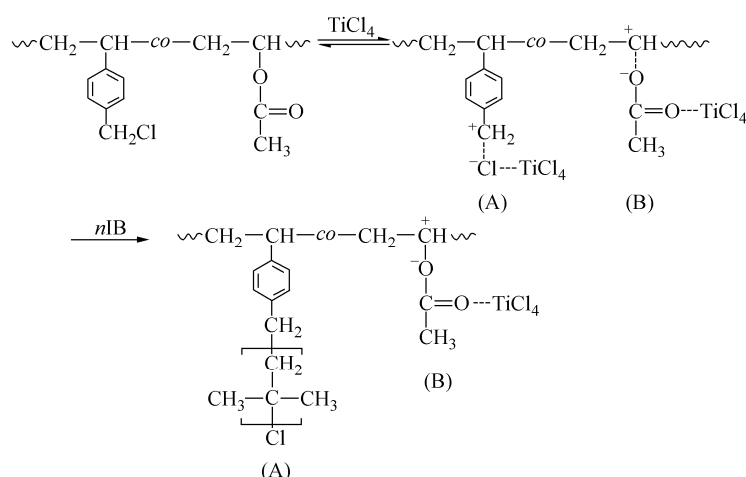
Fig. 2 $^1\text{H-NMR}$ spectrum of the macroinitiator CV_2 (26 mol% VBC) and signal assignment

As presented in Fig. 2, the signals (a_1 , a_2 , a_3) at $\delta=1.39$, 1.77 and 1.86 are assigned to the three different kinds of methylene ($-\text{CH}_2-$) groups along the backbone which are dependant on the sequence in P(VBC-co-VAC) copolymers respectively. The signal (a_1) at $\delta=1.39$ is assigned to $-\text{CH}_2-$ which is adjacent to $-\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$ groups on both sides. The signal (a_2) at $\delta=1.77$ is assigned to $-\text{CH}_2-$ which is adjacent to $-\text{CH}-\text{OOC}-\text{CH}_3$ group and $-\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$ group. The signal (a_3) at $\delta=1.86$ is ascribed to $-\text{CH}_2-$ which is adjacent to $-\text{CH}-\text{O}-\text{CO}-\text{CH}_3$ groups on both sides. Therefore, it can be inferred that the random copolymer P(VBC-co-VAC) of VAC and VBC could be obtained by radical polymerization.

On the basis of the integral values of the characteristic signals at $\delta=4.55$ and $\delta=4.85$, the VBC contents in the P(VBC-co-VAC) copolymer could be calculated according to Eq. (1), and the results are listed in Table 1. The copolymer composition could be mediated by changing the monomer ratio in the feed.

Synthesis of P(VBC-co-VAC)-g-PIB via Cationic Polymerization of IB with P(VBC-co-VAC) Macroinitiator

The synthesis of the graft copolymers P(VBC-co-VAC)-g-PIB was carried out via the grafting cationic polymerization of IB from the random copolymer P(VBC-co-VAC) of VBC and VAC. The copolymers of CV₂, CV₃ and CV₄ with different VBC contents of 25 mol%, 55 mol% and 62 mol% in copolymers respectively were used as macroinitiators. TiCl₄ was selected as a co-initiator to form the active centers, as shown in Scheme 2. The details of the synthesis and experimental results are shown in Table 2.



Scheme 2 Synthesis of the graft copolymer P(VBC-co-VAC)-g-PIB

Table 2. Synthesis of graft copolymer with P(VBC-co-VAC)/IB/TiCl₄ system

No.	Macroinitiator	VBC (mol%)	[TiCl ₄] (mol/L)	[VBC]/[TiCl ₄] (mol/mol)	[IB] (mol/L)	Yield (%)	$M_n \times 10^{-3}$	M_w/M_n
GC ₁	CV ₂	26	0.04	0.10	0.67	100	14	2.1
GC ₂	CV ₂	26	0.04	0.20	0.67	100	12	2.2
GC ₃	CV ₂	26	0.04	0.31	0.67	100	11	2.4
GC ₄	CV ₂	26	0.04	0.37	0.67	100	11	2.4
GC ₆	CV ₃	55	0.05	0.10	0.81	92	22	2.0
GC ₇	CV ₃	55	0.05	0.20	0.81	72	19	2.0
GC ₈	CV ₃	55	0.05	0.60	0.81	85	17	2.3
GC ₉	CV ₃	55	0.05	0.93	0.81	85	15	2.5
GC ₁₀	CV ₄	62	0.04	0.26	0.67	100	19	1.7
GC ₁₁	CV ₄	62	0.04	0.43	0.67	100	17	1.7
GC ₁₂	CV ₄	62	0.04	0.60	0.67	100	16	1.8
GC ₁₃	CV ₄	62	0.04	0.77	0.67	100	16	1.9
GC ₁₄	CV ₄	62	0.04	0.95	0.67	97	17	1.8
GC ₁₅	CV ₄	62	0.04	1.12	0.67	100	17	1.8

Polymerization temperature: -40°C; Polymerization time: 30 min; Solvent: CH₂Cl₂

As shown in Scheme 2, when TiCl₄ was added to the P(VBC-co-VAC) solution in CH₂Cl₂, the strong complex reactions of benzyl chloride with TiCl₄ or acetate group with TiCl₄ took place immediately, leading to the formation of two corresponding active sites (A) and (B) in VBC units and in VAC units respectively. The active site (A) formed more quickly than active site (B) and was more active than active site (B), resulting in initiating the cationic polymerization of isobutylene (IB) mainly from active site (A) to form the graft copolymer P(VBC-co-VAC)-g-PIB. Therefore, TiCl₄ plays an important role in forming the initiating species, and the molar ratio of VBC to TiCl₄ is one of the most important factors to affect the “grafting from” cationic polymerization.

The effect of VBC/TiCl₄ (molar ratio) on monomer conversion, number average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of the resultant copolymers was investigated under 3 sets of conditions by changing the amount of P(VBC-co-VAC) while keeping other conditions constant. As shown in Table 2, high monomer conversions were obtained under all the reaction conditions and molecular weight of all products increased to 4–9 times higher than that of the corresponding macroinitiator. M_n of the graft copolymer P(VBC-co-VAC)-g-PIB reached 22×10^3 under a proper condition (run: GC₆). Furthermore, M_n of the graft copolymer P(VBC-co-VAC)-g-PIB decreased gradually with increasing molar ratios of VBC/TiCl₄, which is attributed to an increase in the initiating active sites.

The representative unimodal GPC traces of the resultant graft copolymers recorded by dual RI and UV detectors are given in Fig. 3. The GPC curve by RI detector is almost in harmony with the GPC curve by UV detector, reflecting that copolymers P(VBC-co-VAC)-g-PIB with relatively narrow MWD (M_w/M_n ca. 2.0) could be successfully synthesized when VBC/TiCl₄ (molar ratio) was set in the range from 0.10 to 1.12, and the copolymerization was conducted at -40°C for 30 min.

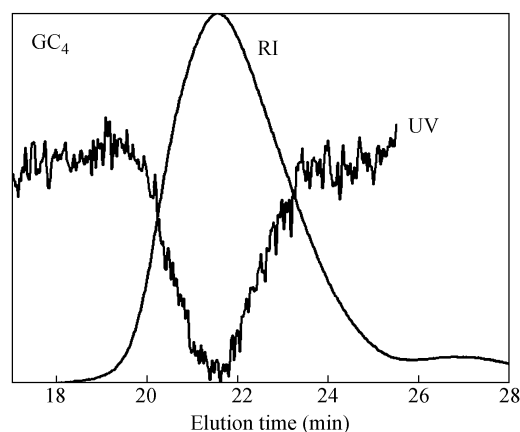


Fig. 3 The representative GPC traces (RI/UV detectors) of the graft copolymer GC₄: $M_n = 11000$, $M_w/M_n = 2.4$; Macroinitiator CV₂: $M_n = 2900$, $M_w/M_n = 2.1$

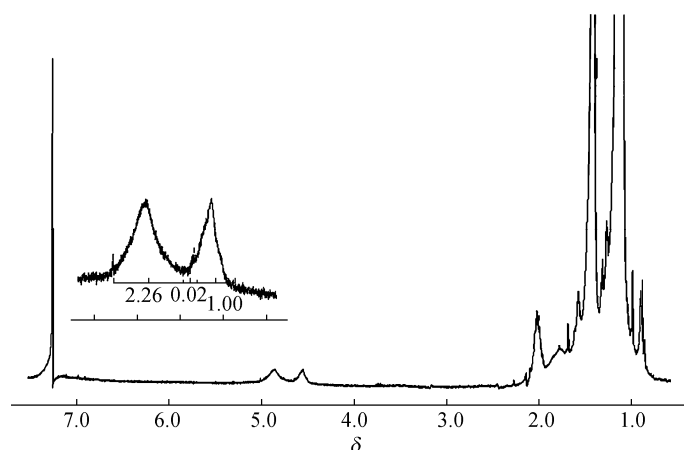


Fig. 4 The representative ^1H -NMR spectrum of the graft copolymer P(VBC-co-VAC)-g-PIB GC₄: $M_n = 11000$, $M_w/M_n = 2.4$; Macroinitiator CV₂: $M_n = 2900$, $M_w/M_n = 2.1$

The representative ^1H -NMR spectrum of the graft copolymers is given in Fig. 4. It can be observed that not all the benzyl chloride groups were efficient to initiate the cationic polymerization of IB since the characteristic signal for $-\text{CH}_2\text{Cl}$ still appeared in the ^1H -NMR spectrum. With respect to the copolymer (run: GC₄) from

macroinitiator CV₂, the ¹H-NMR analysis shows that 31% of the benzyl chloride groups were active as initiating sites for IB polymerization, namely the average branch chains from P(VBC-*co*-VAC) backbone is around 2.1. For the copolymer (run: GC₇) from CV₃, 42% of the benzyl chloride groups were active as initiating sites for IB polymerization, which indicating that P(VBC-*co*-VAC)-*g*-PIB copolymers had, in average, 5.5 PIB branches. Furthermore, the observed signals at $\delta = 1.69$ and 1.96 are assigned to CH_3 and CH_2 in the end groups of *tert*-chloride ($-\text{CH}_2-\text{C}(\text{CH}_3)_2\text{Cl}$) of PIB branch chains respectively. Therefore, the P(VBC-*co*-VAC)-*g*-PIB copolymers with terminal *tert*-chlorine functional groups could be obtained.

In order to provide further experimental evidence for the P(VBC-*co*-VAC)-*g*-PIB copolymers, the representative TEM image of P(VBC-*co*-VAC)-*g*-PIB copolymer is given in Fig. 5. The TEM image indicates that the P(VBC-*co*-VAC)-*g*-PIB copolymer formed a homogeneous two-phase morphology with P(VBC-*co*-VAC)-rich domains (dark phase) of 20–100 nm in size tethered by PIB branch segments (bright continuous phase).

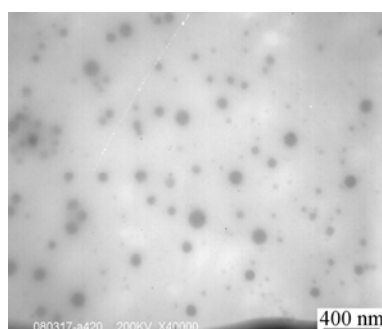


Fig. 5 TEM image of the graft copolymer P(VBC-*co*-VAC)-*g*-PIB (GC₄)

CONCLUSIONS

The random copolymers of poly(4-vinylbenzyl chloride-*co*-vinyl acetate) (P(VBC-*co*-VAC)) with number average molecular weight (M_n) ranging from 2000 to 6900, relatively narrow molecular weight distribution (MWD, M_w/M_n ca. 2.0) could be prepared by radical polymerization using AIBN as an initiator. The different composition of 4-vinylbenzyl chloride (VBC) from 17 mol% to 62 mol% in P(VBC-*co*-VAC) copolymers could be mediated by changing the monomer ration in the feed. The P(VBC-*co*-VAC) copolymers with an average number of 7 to 13 initiating sites of benzyl chloride per macromolecular chain could be used as macroinitiators for the cationic polymerization of isobutylene in conjunction with TiCl_4 at -40°C in CH_2Cl_2 . The molecular weight of all resultant graft copolymers P(VBC-*co*-VAC)-*g*-PIB increased to 4–9 times higher than that of the corresponding macroinitiator, and M_n of the graft copolymer decreased gradually with increasing molar ratios of VBC/ TiCl_4 . It should be pointed that around 31% to 42% of the benzyl chloride groups in P(VBC-*co*-VAC) copolymers were active as initiating sites for IB polymerization. It is found that the graft copolymers P(VBC-*co*-VAC)-*g*-PIB with terminal *tert*-chlorine functional groups in side PIB chains could be successfully synthesized when VBC/ TiCl_4 (molar ratio) was ranging from 0.10 to 1.12. The unimodal GPC curve of the P(VBC-*co*-VAC)-*g*-PIB copolymer by RI detector was almost in harmony with the GPC curve by UV detector. The P(VBC-*co*-VAC)-*g*-PIB copolymer formed a two-phase morphology with P(VBC-*co*-VAC)-rich domains of 20–100 nm in size tethered by PIB branch segments.

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