Synthesis of Poly(vinyl chloride)-*b*-Poly(*n*-butyl acrylate)-*b*-Poly(vinyl chloride) by the Competitive Single-Electron-Transfer/Degenerative-Chain-Transfer-Mediated Living Radical Polymerization in Water

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ABSTRACT: The synthesis of a block copolymer poly(vinyl chloride)-*b*-poly(*n*-butyl acrylate)-*b*-poly(vinyl chloride) is reported. This new material was synthesized by single-electron-transfer/degenerative-chain-transfer-mediated living radical polymerization (SET-DTLRP) in two steps. First, a bifunctional macroinitiator of α,ω-di(iodo)poly (butyl acrylate) [α,ω-di(iodo)PBA] was synthesized by SET-DTLRP in water at 25 °C. The macroinitiator was further reinitiated by SET-DTLRP, leading to the formation of the desired product. This ABA block copolymer was synthesized with high initiator efficiency. The kinetics of the copolymerization reaction was studied for two PBA macroinitiators with number–average molecular weight of 10 k and 20 k. The relationship between the conversion and the number–average molecular weight was found to be linear. The dynamic mechanical thermal analysis suggests just one phase, indicating that copolymer behaves as a single material with no phase separation. This methodology provides the access to several block copolymers and other complex architectures that result from combinations of thermoplastics (PVC) and elastomers (PBA). From industrial standpoint, this process is attractive, because of easy experimental setup and the environmental friendly reaction medium. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 3001–3008, 2006

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INTRODUCTION

Living radical polymerization (LRP) provides an efficient tool for polymer synthesis, yielding macromolecules with controlled molecular weight, narrow polydispersities, and long-lived chains that

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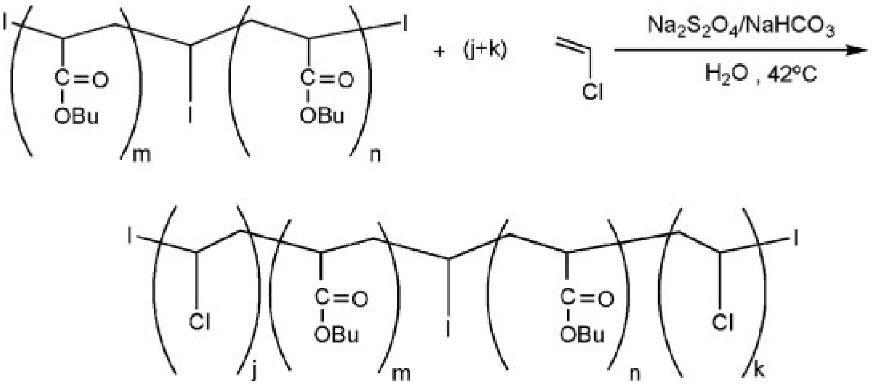


Scheme 1. SET-DTLRP of VC initiated from the α,ω-di(iodo)PBA and catalyzed with $Na_2S_2O_4$ in water at 42 °C.

can be further activated. LRP technique allows to prepare new tailor-made polymers with complex macrostructures that are inaccessible by conventional free radical polymerization method. The main techniques reported in literature are: the transition-metal-catalyzed LRP,[1,2] stable free-radical polymerization[3] reversible addition–fragmentation chain-transfer polymerization,[4] and degenerative transfer (DT).[5]

Percec et al.[6–8] discovered a new methodology named as single-electron-transfer/degenerative-chain-transfer living radical polymerization (SET-DTLRP). This method provides the reversible activation–deactivation step required to accomplish LRP by a combination of competitive single-electron-transfer (SET) and degenerative-chain-transfer (DT) mechanisms. This strategy has proved to be effective in the polymerization of activated[9,10] and nonactivated monomers.[8,11–14] The ability to synthesize block copolymers made with acrylates using LRP methodologies is extremely important from different standpoints. First, it is possible to control the polymerization of different monomers with very high polymerization rates, the preparation of materials with different morphologies and resistance to different chemical environments, and the study of the influence of polymers with different natures on the mechanical properties. For the specific block copolymer synthesis present in this work, this material is important for commercial purposes, since it opens the possibility to prepare flexible materials based on PVC without the using of common free plasticizers.[15] The migration of plasticizers from the PVC matrix is one of the most serious problems encountered in the packaging technology, especially for products such as food and pharmaceuticals.[16]

In this work, we report the use of α,ω-di(iodo)-poly(butyl acrylate) [α,ω-di(iodo)PBA] macroinitiators for the SET-DTLRP of VC catalyzed with $Na_2S_2O_4$ at 42 °C in water[8] to produce the ABA block copolymer PBA-*b*-PVC-*b*-PBA. The copolymer was characterized by NMR, FTIR, size exclusion chromatography (TriSEC), dynamical mechanical thermal analysis (DMTA), and TGA.

RESULTS AND DISCUSSION

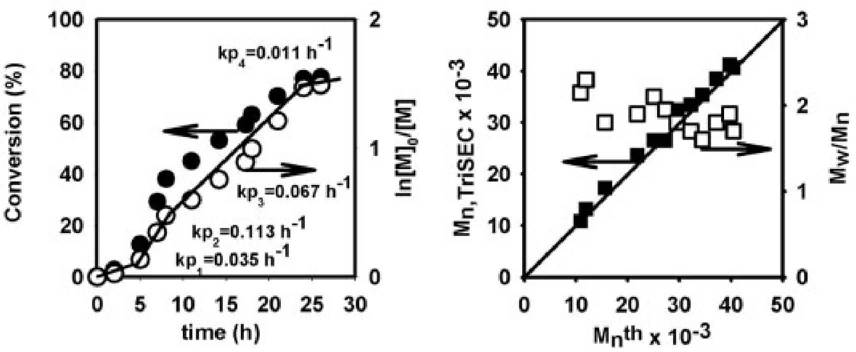
Synthesis of PVC-*b*-PBA-*b*-PVC by the SET-DTLRP of VC Initiated from α,ω-Di(iodo)PBA Macroinitiator

Two α,ω-di(iodo)PBA macroinitiators with different $M_{n,\mathrm{TriSEC}}$ were used as starting materials to determine the role of the initial $M_{n,\mathrm{TriSEC}}$ in the copolymerization kinetics.

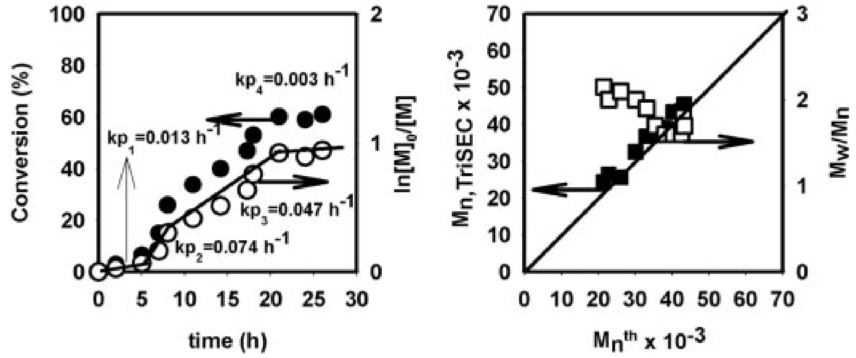
The block copolymer was synthesized by SET-DTLRP of VC initiated from the α,ω-di(iodo)PBA and catalyzed with $Na_2S_2O_4$ in water at 42 °C (Scheme 1).

Methocel F50 and poly(vinyl alcohol) (PVA88), which was 87–89% hydrolyzed and has a weight–average molecular weight (M_w) of 124,000–186,000, were used as suspension agents. The block copolymer experiments were carried out in 50-mL glass pressure tubes. The kinetics of copolymerization was determined for two macroinitiators. Each point of the kinetic curve corresponds to a single experiment performed at exactly the same conditions and different reaction times. At the end of the reaction, the copolymer was washed with deionized water, filtered, and dried under vacuum at 25 °C until constant weight was reached. The conversion was determined gravimetrically.

The kinetic of the copolymerization with the macroinitiator with lower $M_{n,\mathrm{TriSEC}}$ was performed under the following conditions: $[VC]_0/[PBA]_0/[Na_2S_2O_4]_0/[p\mathrm{TsNa}]_0/[NaHCO_3]_0 = 600/1/$



a) $[VC]_0/[PBA]_0/[Na_2S_2O_4]_0/[pTsNa]_0/[NaHCO_3]_0$=600/1/8/4/1.45



b) $[VC]_0/[PBA]_0/[Na_2S_2O_4]_0/[pTsNa]_0/[NaHCO_3]_0$=400/1/8/4/1.45

Figure 1. Dependence of $M_{n,\mathrm{TriSEC}}$ and ln M_0/M on the conversion for the $Na_2S_2O_4$-catalyzed copolymerization of PVC-*b*-PBA-*b*-PVC at 42 °C under the following conditions: (a) $[VC]_0/[PBA]_0/[Na_2S_2O_4]_0/[pTsNa]_0/[NaHCO_3]_0$ = 600/1/8/4/1.45 (mol/mol/mol/mol) and [MethocelF50]/[PVA 88] = 1260/2940 (ppm/ppm, w/w relative to VC); $[VC]_0/[PBA]_0/[Na_2S_2O_4]_0/[pTsNa]_0/[NaHCO_3]_0$ = 400/1/8/4/1.45 (mol/mol/mol/mol) and [MethocelF50]/[PVA 88] = 1260/2940 (ppm/ppm, w/w relative to VC).

8/4/1.45 (mol/mol/mol/mol) and [MethocelF50]/[PVA 88] = 1260/2940 (ppm/ppm, w/w relative to VC) at 42 °C [Fig. 1(a)]. The kinetic plot shows the existence of an induction period, presumably ascribed to the necessary time to dissolve the PBA macroinitiator by the VC, decreasing the viscosity of the medium and conducting to the activation of the iodine chain ends. Once the PBA dissolution is complete, the block copolymerization presents four main kinetic rates: the first one is relatively slow (k_{p1} = 0.035 h^{-1}), followed by the faster reactions (k_{p2} = 0.113 h^{-1}), the third one that appears for longer time (k_{p3} = 0.067 h^{-1}), and finally the last one, where the reaction almost stops (k_{p4} = 0.011 h^{-1}). The first step, between 3 and 17% of conversion, is related to the activation of the iodine chain ends following the mechanism described elsewhere.[8] The increase of the radical concentration in conjunction with the low reaction viscosities presented in this stage justifies the higher rate of copolymerization compared with that of the other three stages. During this period, it forms a suspension phase, with the unavoidable enhancement of viscosity, that leads to the third stage of polymerization. Finally, the precipitation of the polymer, which was observed after 24 h of reaction, causes the decrease of the copolymerization rate. The living character of this block copolymerization is confirmed by the close agreement between the M_n^{th} (or conversion) and the $M_{n,\mathrm{TriSEC}}$ obtained by TriSEC.

The second kinetic experiment was done with α,ω-di(iodo)PBA macroinitiator ($M_{n,\mathrm{TriSEC}}$ = 20,300 and M_w/M_n = 2.2) under the following conditions:

$[VC]_0/[PBA]_0/[Na_2S_2O_4]_0/[pTsNa]_0/[NaHCO_3]_0$ = 400/1/8/4/1.45 (mol/mol/mol/mol) and [MethocelF50]/[PVA 88] = 1260/2940 (ppm/ppm, w/w relative to VC) at 42 °C [Fig. 1(b)].

The kinetic behavior of this copolymerization resembles the kinetic behavior described for the first macroinitiator. The induction period seems to be more pronounced, which may be related to the

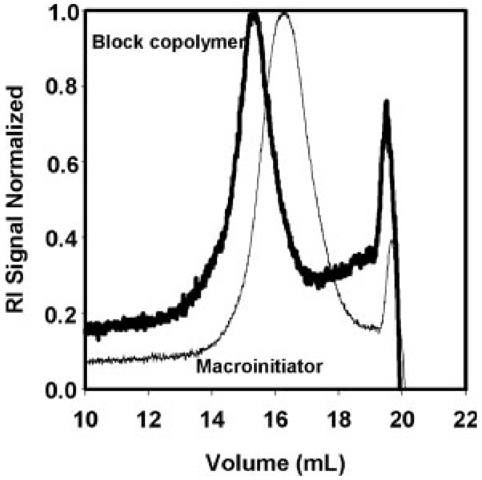


Figure 2. RI trace of the macroinitiator α,ω-di(iodo) PBA and the block copolymer PVC-*b*-PBA-*b*-PVC prepared by SET-DTLRP of VC in water at 42 °C.

higher $M_{n,TRiSEC}$ of the macroinitiator. In this case, the dissolution of PBA by the VC requires longer times. Another important observation is the fact that the transitions between the different polymerization stages occur at very similar reaction times, although the maximum conversion obtained for the last stage is lower in this second kinetic. Again, the M_n^{th} matches the molecular weight determined experimentally, and it is observed that there is a decrease of M_w/M_n during the reaction until the formation of the solid phase. Ideally, the M_w/M_n should decrease with the increasing $M_{w,TriSEC}$ (reaction time) at least for homogeneous systems, although in heterogeneous reaction medium this cannot be the case, since the diffusional limitations avoid the equal distribution and diffusion of monomer through the reaction media. This behavior was also observed for the SET-DTLRP of BA.[17]

Figure 2 shows the RI trace of the macroinitiator α,ω-di(iodo) PBA ($M_{n,TriSEC} = 10,835$) and the block copolymer PVC-*b*-PBA-*b*-PVC prepared by SET-DTLRP of VC at 42 °C after 26 h of reaction (77.5% of conversion).

The RI traces show the total movement of the molecular weight toward higher molecular weights, which indicates high initiation efficiency.

Thermal Analysis

The DMTA is one the most main techniques to study the mechanical and thermal properties of the polymers. Figure 3 shows the temperature dependence of tan δ of α,ω-di(iodo) PBA and α,ω-di(iodo)poly(vinyl chloride) [α,ω-di(iodo)PVC] prepared under the same conditions used in the reinitiation step (42 °C), and that of block copolymer PVC-*b*-PBA-*b*-PVC. The peak at the maximum value in tan δ corresponds to glass transition temperature, which is controlled by both intra- and intermolecular interactions. In systems with phase separation, the molecular motions of each component remain unchanged, whereas in miscible blends, the motions are strongly affected and a single sharp peak appears.[18] PBA shows a peak at −43 °C. This peak is ascribed to α-relaxation corresponding to glass transition and reflects the motions of the long chain segments in the amorphous domains of PBA. On the other hand, the neat PVC has a distinct T_g at 90 °C. Typically, the T_g is 80 °C for the PVC prepared by conventional free-radical polymerization. Such difference might be due to higher syndioctacticity of PVC segments obtained with the SET-DTLRP process.[8] Concerning the block copolymer, it is possible to observe only one peak at temperature (25 °C) that is located between the T_g of the homopolymers. This observation is generally accepted as an indication of interaction between the pure polymers at the molecular level. From this information, two main aspects should be stressed. Firstly, the absence of any defined peak at −43 °C indicates that the initiation efficiency should be close to 100%, otherwise the unreacted α,ω-di(iodo)PBA should have produced a single pronounced peak. Secondly, the PVC formed after the reinitiation is linked to PBA shows that no chain-transfer reaction to monomer occurred during the VCM polymerization at 42 °C. The broadened glass-transition region suggests some heterogeneity in the copolymer constitution, possibly

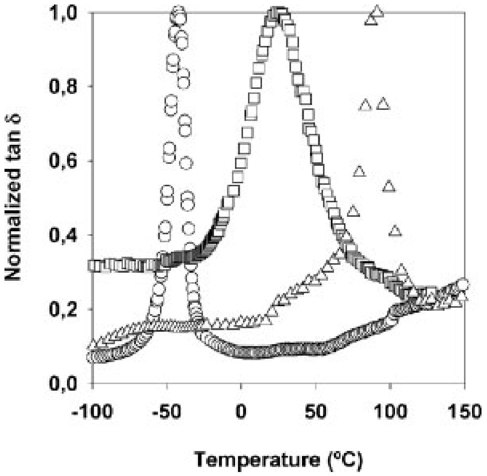


Figure 3. Normalized tan δ for (○) PBA, (□) PVC-*b*-PBA-*b*-PVC, and (△) PVC prepared by SET/DTLRP.

Table 1. Structural, Viscosimetric and Thermal Characterization of PVC-*b*-PBA-*b*-PVC

No.	Block Copolymer $M_{n,\mathrm{TriSEC}}$	PVC[a] (wt %)	PBA (wt %)	η (dL/g)	dn/dc	R_g (nm)	Theoretical T_g (°C)	Experimental T_g (°C)
0	10.859	–	100	0.1537	0.064	4.563	–	−43
1	17.325	44	56	0.2468	0.068	6.292	11	5.4
2	23.623	64	36	0.4274	0.072	8.1159	25	24
3	26.543	70	30	0.4051	0.076	8.5267	35	26
4	26.499	68	32	0.4434	0.082	9.0105	33	27
5	32.432	78	22	0.4831	0.085	9.629	49	56
6	27.467	100	–	0.750	0.105	9.56	–	90

[a] Determined by ^{1}H NMR.

due to the presence of PVC chains with different lengths in copolymer. This result is typically observed when a system is under deficient stirrer conditions that generally contribute to problems related to monomer movements in the reaction medium. A narrowing of the α-relaxation region for high-scale regions due to the more stringent control of the thermal and mixing phenomena should be expected in comparison with the stirrer capacity of the magnets used in the 50 mL glass reactors. The T_g value of 24 °C for the copolymer (No. 2, Table 1), as referred before, is between the T_g's of the homopolymers and it is relatively close to the theoretically value calculated using the Fox equation, $1/T_g = W(\mathrm{PBA})/T_g\,(\mathrm{PBA}) + W\,(\mathrm{PVC})/T_g\,(\mathrm{PVC})$, where T_g is the glass transition temperature of block copolymer, W(PBA) and T_g (PBA) are the weight fraction and the glass transition temperature of PBA, respectively, and W(PVC) and T_g (PVC) are the corresponding values of PVC, assuming that PVC and PBA are miscible. This behavior was also observed by Percec et al. for the block copolymer poly(vinyl chloride)-*b*-poly(2-ethyl hexyl acrylate)-*b*-poly(vinyl chloride).[19]

The thermogravimetric curves of these three samples are presented in Figure 4. The copolymer prepared is thermostable, and there is some interaction between the PBA and PVC segments since the first degradation step that corresponds to the PVC segment of the copolymer is slightly retarded. As expected, the PBA is the polymer with higher themostability.

Structural Analysis of the PBA by 500-MHz ^{1}H NMR and FTIR Spectroscopy

The NMR spectrum of the PBA obtained by SET-DTLRP of BA at 25 °C and the block copolymer PVC-*b*-PBA-*b*-PVC are presented in Figure 5. The PBA macroinitiator spectra [Fig. 5(a)] shows the signals expected for the SET-DTLRP of BA, which were identified and ascribed in a previous publication.[17] Figure 5(b) shows the disappearance of the signal at 5.0 ppm that corresponds to the *r* and *m* stereoisomers of —CHIC(O)OBu active chains ends. This process conducted to the formation of the block copolymer PVC-PBA-PVC. The success of this block copolymerization can be confirmed by the presence of peaks characteristic of PVC (—CHCl between 4.2 and 4.5 ppm and CH_2 between 2.0 and 2.5 ppm). Because of low concentration of *r* and *m* —CHCHlI end groups of PVC moieties, their resonances at 6 ppm[8] were not observed.

Figure 6 shows the FTIR spectra of PVC and the block copolymer PVC-*b*-PBA-*b*-PVC in the

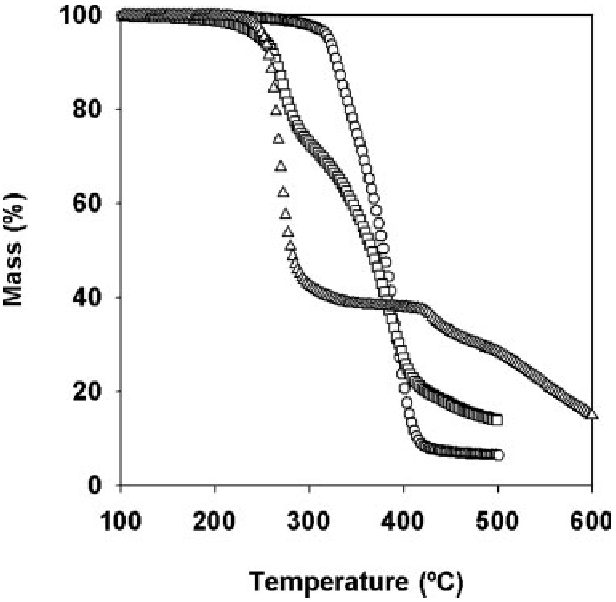


Figure 4. TGA traces for (○) PBA, (□) PVC-*b*-PBA-*b*-PVC, and (△) PVC prepared by SET/DTLRP.

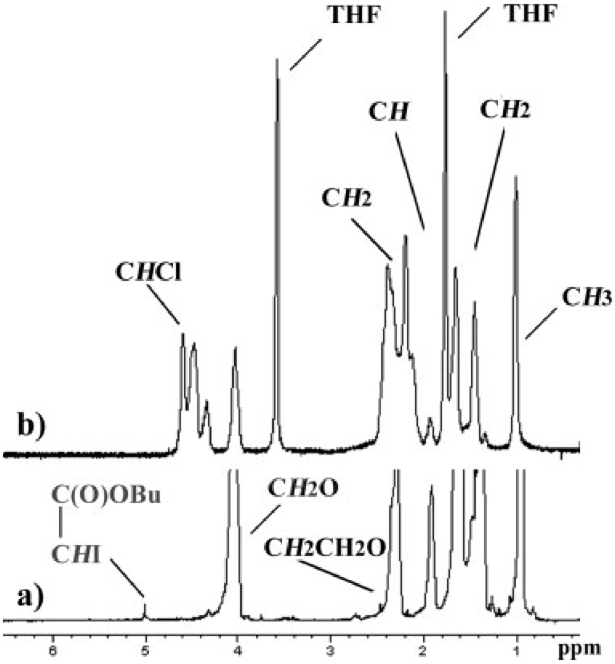


Figure 5. 500-MHz ^{1}H NMR (a) of the macroinitiator α,ω-di(iodo)PBA and (b) the block copolymer PVC-*b*-PBA-*b*-PVC prepared by SET/DTLRP.

wavelength range of 4000–400 cm^{-1}. The FTIR spectra of the block copolymers shows characteristics absorption peaks of the two polymers involved, supporting its formation. The peaks are at 1727 cm^{-1} (ascribed to C=O of carbonyl group of PBA), 1440 cm^{-1} (ascribed to δCH_2 of PVC), 1243 cm^{-1} (ascribed to δCH of PVC), 1160 cm^{-1} (ascribed to υC-O of PBA), 940 cm^{-1} (ascribed to υCH_2 of PVC), and 616 cm^{-1} (ascribed to υC—Cl of PVC).[20]

Some of the prepared block copolymers were selected according to their compositions and molecular weights, and the results are presented in Table 1.

The results summarized in Table 1 show that the incorporation of PVC leads to an obvious increase of the T_g. The other viscosimetric parameters as the η, dn/dc, and R_g also reveal a notorious increase.

An important property to be evaluated for any block copolymer is its purity. The sources of impurities in this specific system potentially are the unreacted α,ω-di(iodo) PBA and PVC that may be formed from chain-transfer reactions to the monomer during the second stage of polymerization.

Based on the main results presented in this work—the existence of only one peak in the DMTA trace of the block copolymer, the initiator efficiency; the lack of evidence of any low molar mass corresponding to the initial macroinitiator; and considering that the copolymer was rinsed only with water that naturally is not the solvent of PVC or PBA, we could suggest that the copolymer is free of homopolymers. This conclusion was expected because of the level of control achieved by this method for extremely reactive monomers with very high propagation rate.[8]

CONCLUSIONS

The block copolymer PVC-*b*-PBA-*b*-PVC was successfully synthesized by SET-DTLRP of VC initiated from α,ω-di(iodo)PBA and catalyzed by $Na_2S_2O_4$ in H_2O at 42 °C. The DMTA traces indicate that the copolymer presents just one phase regardless of the amount of PVC incorporated in the PBA. Furthermore, the glass transition temperatures of the block copolymers are in good agreement with the theoretically calculated values by the Fox equation. The presence of only one peak for all the copolymers prepared, considering the broad range of compositions studied, is remarkable. Moreover, other studies with blending technologies showed the incapacity to prepare copolymers that behave as a single material for a wide range of composition due to miscibility problems.[21] These results are extremely promising

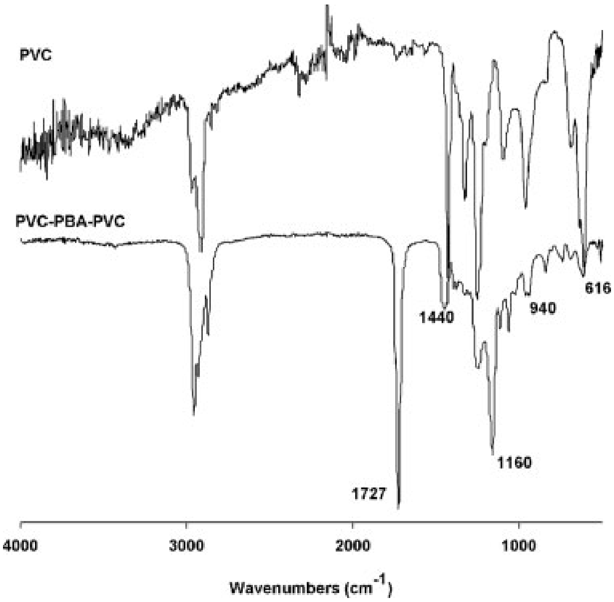


Figure 6. FTIR spectrum of PVC and PVC-*b*-PBA-*b*-PVC prepared by SET/DTLRP in water.

considering the replacement of the PVC mixed with plasticizers by these new flexible products.

EXPERIMENTAL

Materials

The tetrahydrofuran HPLC-grade uninhibited, sand, alumina oxide, iodoform (99%), sodium dithionate (85%), sodium bicarbonate (99%), and BA were purchased from Sigma-Aldrich. The BA was purified through a basic Al_2O_3 column. The polystyrene standards were purchased from Polymer Laboratories. The hydroxypropyl methylcellulose, Methocel F50, was purchased from Dow Chemical Company. The partially hydrolyzed poly (vinyl alcohol) (PVA) was purchased from Syntomer. The VC was purchased form ShinEtsu and used as received. The deuterated solvents were ordered from Cortecnet.

Synthesis of α,ω-Di(iodo)polyBA Macroinitiator

The α,ω-di(iodo)PBAs were synthesized in a 2-L reactor by SET-DTLRP of BA initiated with iodoform in H_2O at 25 °C, according to the procedure described in literature.[17,22] Two PBAs with number–average molecular weight were synthesized. The first one had a $M_{n,\mathrm{TriSEC}}$ of 10,835 and M_w/M_n of 2.32, whereas the second one had a $M_{n,\mathrm{TriSEC}}$ of 20,300 and M_w/M_n of 2.31. The DMTA traces of these two polymers indicate a glass transition temperature (T_g) of −43 °C.

Synthesis of α,ω-Di(iodo)poly(vinyl chloride)

The α,ω-di(iodo)PVC was synthesized by SET-DTLRP of VC initiated with iodoform in H_2O at 42 °C, according to the procedure described in literature.[8] This polymer was used for thermal comparison with the block copolymer PVC-*b*-PBA-*b*-PVC, and for that reason it was synthesized under the same conditions used for the reinitiation of the macroinitiators α,ω-di(iodo)PBA.

Typical Procedure to Synthesize the Block Copolymer PVC-*b*-PBA-*b*-PVC by the SET-DTLRP of VC Initiated from α,ω-Di(iodo)PBA Macroinitiator

In a 50-mL Ace Glass 8645#15 pressure tube equipped with bushing and plunger valve was charged 16 mL of desionized water, 678.92 mg of 3% water solution of PVA (2940 ppm w/w relative to VC), and 469.30 mg of 1.86% water solution MF50 (1260 ppm w/w relative to VC). The content was stirred and bubbled with nitrogen for 10 min. The other compounds were then weighted, and catalyst ($Na_2S_2O_4$; 144.98 mg, 0.148 mmol), macroinitiator (α,ω-di(iodo)PBA; 2.00 g, 0.018 mmol), buffer ($NaHCO_3$; 31.04 mg, 0.037 mmol), *p*-toluene sulfuric acid (*p*TsNa; 144.98 mg, 0.074 mmol) were added to the tube. The tube was frozen in MeOH/dry ice, and precondensed VC (7.87 mL, 0.11 mol) was added. The reactor was closed and degassed through the plunger valve by applying circles of reduced pressure followed by filling the tube with inert gas for 20 times at −40 °C. The valve was closed and the reaction was kept in a controlled temperature water-bath for different reaction times. At the end of the reaction, the excess of unreacted VC was distilled and the block copolymer was filtered and rinsed three times with desionized water. After dying in a vacuum oven until constant weight was reached, the block copolymers were characterized.

Sample Preparation for Size Exclusion Chromatography (TriSEC)

Around 40 mg of the block copolymer was allowed to complete dissolution in a dilution flask of 10 mL over 24 h. The solution was passed through a basic Al_2O_3 column, precipitated in water and filtered under vacuum. The polymer was then dried in the oven at 40 °C under vacuum until constant weight was reached. Approximately 20 mg of the block copolymer were dissolved in 10 mL of THF under stirring for 24 h. The exact concentration was determined considering the weight measured and the 10 mL of solvent used (all the samples were prepared with concentrations around 2 mg/mL).

Characterization Techniques

The chromatography parameters of the samples were determined using a HPSEC, Viscotek (Dual detector 270, Viscotek, Houston, USA) with a differential viscometry (DV), right angle laser light scattering (RALLS, Viscotek), and RI (Knauer K-2301). The column set consisted of a PL 10-μm guard column (50 × 7.5 mm^2) followed by two Mixed-B PL columns (300 × 7.5 mm^2, 10 μm). HPLC pump (Knauer K-1001) was set with a flow rate of 1 mL/min. The eluent (THF) was previously filtered through a 0.2-μm filter. The system was also equipped with a Knauer online degasser.

The tests were done at 30 °C using an Elder CH-150 heater. Before the injection (100 μL), samples were filtered through a PTFE membrane of 0.2 μm. The system was calibrated with narrow polystyrene standards. The differential refractive index (dn/dc) for 670 nm was determined for each copolymer by TriSEC. The analysis of light scattering data by Viscotek's software was done assuming that the second virial coefficient was zero, considering the low solution concentrations used in this work. FTIR spectra were obtained in a Nicolet 750, using a Golden Gate ATR accessory from Specac, where the products were analyzed as prepared. Resolution was 4 and the number of scans was 64. The ^{1}H NMR spectra (500 MHz) were recorded in a Bruker DRX 500 spectrometer at 32 °C in $CDCl_3$ with tetramethylsilane as internal standard and THF-d_8.

DMTA of thick specimens (15.20 mm × 7.45 mm × 1.2 mm) were performed by a Triton Tritec 2000 in the constrain layer damping mode using a frequency of 1 Hz, with a standard heating rate of 5 °C/min. The T_g was determined as the peak in tan δ ($\tan \delta = E''/E'$), where E'' and E' are the loss and storage moduli, respectively. The TGA curves were determined using a Netzsch STA 449C Jupiter and the tests were carried out at 5 °C/min.

Calculation of Intrinsic Viscosity [η] and Molecular Weight [M_w]

The parameters presented in this work (M_n, number–average molecular weight; M_w, weight–average molecular weight; η, intrinsic viscosity; R_g, gyration radius) were calculated using the TriSEC software provided by Viscotek (version 3.0). The algorithm applied in the software is briefly described in literature,[23] and it will not be repeated here again. It should also be referred that the software monitors the elution times of the RALLS, DV, and RI detectors and adjusts the volume calculation according to the RI detector.

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