

Polycarbonate/Clay Nanocomposites via in Situ Melt Polycondensation

Mallikarjuna S. Rama and Sivaram Swaminathan*

Division of Polymer Science and Engineering, National Chemical Laboratory, Pune-411008, Maharashtra, India

Polycarbonate (PC)/clay nanocomposites were prepared via in situ melt polycondensation using novel organoclays modified using phosphonium and imidazolium based cations. The molecular weight of the separated polymer separated from the nanocomposites reveals that phosphonium ion modified organoclays catalyze the polycondensation of bisphenol A with diphenyl carbonate. Wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) indicated that exfoliated polycarbonate/clay nanocomposites could be obtained using organoclays which have reactive bisphenol functionality in the modifier. The glass transition temperature (T_g) of the nanocomposites was studied using differential scanning calorimetry (DSC). The use of a more thermally stable modifier did not improve the color in polycarbonate clay nanocomposites. Although an approach to produce fully exfoliated PC nanocomposites are evident from this study, the process is far from perfect from the point of producing a color free transparent PC.

1. Introduction

Polycarbonates (PCs) possess high impact strength, good optical clarity, and high heat distortion temperature. However, they suffer from the disadvantages of poor chemical resistance and low resistance to abrasion.¹ Thermal properties of polymers are known to be improved by addition of inorganic fillers.² One advantage a filler could contribute to PC would be scratch resistance and surface gloss, and if one could do that without sacrificing the extraordinary optical clarity and toughness of PC, many commercial applications would follow. However, use of traditional fillers often leads to loss of optical property. The possibility of further increasing heat distortion temperature and glass transition temperature (T_g) of PC without impairing its ductility is a continuing research challenge.

Polymer/clay nanocomposites based on layered silicates like montmorillonite have been widely studied during the last 10 years. Because of the high aspect ratio and surface area of the dispersed layered materials, dramatic improvements in the properties of the polymer can be achieved at very low filler levels.^{3–8} Nanocomposites are prepared by three general methods. These are (a) intercalation of polymer or prepolymer from solution (b) in situ intercalative polymerization, and (c) melt intercalation.⁹ The resulting structures may be agglomerated microcomposites or intercalated or exfoliated nanocomposites. The nature of the organoclay as well as the polymer and the method of its preparation determine the structure. Of these, the in situ intercalative polymerization method allows significant opportunities to alter the structure and morphology of nanocomposites.

Many attempts have been made toward preparation of PC/clay nanocomposites. Brittain et al. reported the preparation of partially exfoliated PC/clay nanocomposites using cyclic carbonate oligomers and ditallowdimethyl ammonium modified montmorillonite.¹⁰ Several reports are available for the preparation of PC nanocomposites by melt mixing.^{11–26} Paul and co-workers studied the effect of organoclay structure and molecular weight of PC on morphology and properties of PC/clay nanocomposites using a variety of organoclays.¹¹ Reduction in molecular weight and color formation was observed during melt processing and was shown to be dependent on residence time in the extruder, chemical structure of the modifier, and the iron

content in the silicate clay.¹² Dispersion of organoclay in various polymer blends based on PC like PC/poly(caprolactone) (PCL) blends, PC/poly(methyl methacrylate) blends, and PC/poly-(acrylonitrile-butadiene-styrene) blends were explored to exploit the advantage of combining the properties of a nanocomposite with that of a blend.^{13–18} Attempts have also been made to improve dispersion of clay in PC nanocomposites by use of various compatibilizers such as bisphenol A-diglycidyl ether,¹⁹ maleic anhydride-*g*-polypropylene,²⁰ and poly(styrene-*co*-maleic anhydride).^{21,22} However, complete exfoliation of clay in the PC matrix was not achieved. Lee et al. prepared partially exfoliated PC nanocomposites based on organoclay, Cloisite 25A, by solid-state polymerization induced by microwave heating.²⁷

Most of the studies on PC/clay nanocomposites used quaternary ammonium containing modifiers. However, at the temperature of preparation of PC by melt polycondensation, quaternary ammonium compounds are likely to decompose via the Hoffman elimination reaction, resulting in the formation of *t*-amines.²⁸ Amines are known to induce base catalyzed chain scission of PC leading to molecular weight reduction and color formation.^{11,12,29} One approach to mitigate this problem is to use modifiers which are more thermally stable. Organocations based on phosphonium, imidazolium, and tropylium cations are reported to be stable even at 300 °C.^{30–32} Preparation of PC nanocomposites using phosphonium ion modified montmorillonite was reported to lead to improvement in the thermal stability for PC/clay nanocomposites.³³

It is generally recognized that the properties of the nanocomposite are enhanced when the interaction of the polymer chain with the surface of the clay layer is improved. This can be achieved by chemically tethering the polymer onto the surface of the clay layers which are completely delaminated and fully exfoliated through out the polymer matrix. Many examples of hydrophobic modifiers possessing functional groups capable of copolymerization or initiating polymerization have been recently reported with attendant improvement in the property of nanocomposites.^{34–39} However, there is no report in the literature of a similar approach toward the preparation of PC/clay nanocomposites.

In this paper, we describe the preparation of PC nanocomposites via in situ melt polycondensation using organoclays which have been modified using thermally stable modifiers.

* To whom correspondence should be addressed. E-mail: s.sivaram@ncl.res.in.

Additionally, the modifier also had reactive bisphenol functionality capable of copolymerization with the growing polymer chain during polycondensation. For purposes of comparison, PC nanocomposites were prepared under similar conditions with two organoclays, which are thermally stable but do not contain reactive groups. The molecular weights of polymer and dispersion of clay in the nanocomposites obtained were discussed.

2. Experimental Section

2.1. Materials. Na⁺ montmorillonite was obtained from Southern Clay Products, USA. Methyl acetoacetate and phenol were obtained from Sd Fine Chemicals, Mumbai, India. 1,10-Decanediol, carbon tetrabromide, triphenylphosphine, lithium aluminum hydride, tetramethylammonium hydroxide (TMAH), 1,2-dimethyl imidazole, and 1-hexadecyl bromide were obtained from Aldrich, USA, and were used without further purification. Bisphenol-A and diphenyl carbonate were kindly provided by GE John F. Welch Technology Centre, Bangalore, India.

2.2. Synthesis of 10-Bromodecanol (1). To a mixture of 1,10-decanediol (35.73 g, 0.205 mol) and toluene (700 mL) was added concentrated HBr (29 mL of 47% aqueous solution, 0.24 mol). The heterogeneous mixture was stirred and heated at reflux for 36 h. Thin-layer chromatography (TLC) analysis indicated substantial amounts of 1,10-decanediol still remained. Therefore, a further quantity of HBr (15 mL, 0.12 mol) was added, and the mixture was heated at reflux for a further period of 36 h, at which time TLC analysis showed no diol remaining. The reaction mixture was allowed to cool to room temperature, and the phases were separated. The organic layer was concentrated by evaporating the toluene, diluted with ethyl acetate, and washed with water, sodium bicarbonate, and brine. Then, the organic layer was dried over Na₂SO₄ and concentrated to a yellow liquid. Purification of the crude reaction mixture by column chromatography yielded pure 10-bromodecanol **1** (43.0 g). Yield: 90%. ¹H NMR: 1.2 to 1.8 (18 H, m); 3.43 (2H, t); 3.65 (2H, t).

2.3. Synthesis of Methyl-(3-hydroxydecyl)acetoacetate (2). Clean dry sodium (9.5 g, 0.413 mol) was placed in a three neck round-bottom flask fitted with a double surface condenser, dropping funnel, and septum adapter. Dry methanol (200 mL) was added to the sodium slowly under cooling. Methyl acetoacetate (48.3 g, 0.416 mol) was added under stirring and heated gently. Potassium iodide (5.6 g, 0.033 mol) was added. 10-Bromodecan-1-ol **1** (79 g, 0.33 mol) was placed in a dropping funnel and added slowly into the contents of the round bottomed flask over a period of 60 min. Reflux was continued for 12 h, and the progress of the reaction was monitored by TLC. The reaction was terminated when all the bromodecanol was consumed. The crude reaction mixture was concentrated by evaporating methanol, diluted with ethyl acetate, and washed with water several times until the washings were neutral to litmus. Methyl-(3-hydroxydecyl)acetoacetate **2** (58.3 g), a pale yellow liquid, was separated from the crude product by flash chromatography. Yield: 65%. ¹H NMR: 1.26 to 1.8 (3H, s); 2.23 (3H, s); 3.43 (1H, t); 3.64 (2H, t); 3.74 (3H, s).

2.4. Synthesis of 13-Hydroxytridecan-2-one (3). Methyl-(3-hydroxy decyl)acetoacetate **2** (54.4 g, 0.20 mol) was dissolved in dimethyl sulfoxide (150 mL) in a round-bottom flask, and NaCl (15 g, 0.25 mol) was added to it along with distilled water (18 g, 1.0 mol). The above mixture was heated at 150 °C for 18 h. The reaction was continued until all the starting material was consumed which was monitored by TLC. The product was poured into water and extracted with diethyl ether. The combined ether layer was washed with water and brine and then

dried over sodium sulfate. The ether was evaporated to yield 13-hydroxytridecan-2-one **3** (32.1 g) as a white solid, which is then purified by recrystallization in hot petroleum ether. Yield: 75%. Melting point: 58 °C. ¹H NMR: 1.26 to 1.8 (18H, m); 2.14 (3H, s); 2.42 (2H, t); 3.64 (2H, t).

2.5. Synthesis of 2,2-Bis(4-hydroxyphenyl)tridecanol (4). 13-Hydroxytridecan-2-one **3** (21.4 g, 0.10 mol) was mixed with phenol (56.4 g, 0.60 mol) and mercaptopropionic acid (0.106 g, 0.010 mol). Anhydrous HCl gas was bubbled into the reaction mixture. The reaction was continued under stirring for 12 h at 45 °C. The reaction mixture was dissolved in ethyl acetate and was washed with water, NaHCO₃, and brine. The organic layer was dried over Na₂SO₄. Excess phenol in the reaction mixture was distilled out under vacuum at 60 °C. 2,2-Bis(4-hydroxyphenyl)tridecanol **4** (25.0 g) was purified and isolated by column chromatography as a viscous liquid. Yield: 65%. ¹H NMR: 1.14 to 1.53 (14H, m); 1.57 (3H, s); 1.63 (2H, m); 1.77 (2H, m); 2.00 (2H, m); 4.08 (2H, t); 6.68 (4H, d); 6.93 (4H, d).

2.6. Synthesis of 2,2-Bis(4-hydroxyphenyl)tridecyl Bromide (5). 2,2-Bis(4-hydroxyphenyl) tridecanol **4** (22.37 g, 0.050 mol) and CBr₄ (19.92 g, 0.060 mol) were dissolved in dry tetrahydrofuran (100 mL) and taken in a three-neck round-bottom flask fitted with an additional funnel, condenser, and a three-way stopcock. Triphenylphosphine (14.41 g, 0.055 mol) was dissolved in tetrahydrofuran and added dropwise to the reaction mixture, kept at 0 °C over a period of 30 min. Stirring was continued for another 4 h at 0 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the crude reaction mixture was concentrated by evaporating the solvent. The crude mass was dissolved in ethyl acetate and washed with water. 2,2-Bis(4-hydroxyphenyl)tridecyl bromide **5** (20.1 g) was isolated as a white solid after column chromatography. Yield: 90%. Melting point: 82 °C. ¹H NMR: 1.14 to 1.53 (16H, m); 1.55 (3H, s); 1.84 (2H, m); 1.98 (2H, m); 3.40 (2H, t); 6.68 (4H, d); 6.93 (4H, d).

2.7. Synthesis of 2,2-Bis(4-hydroxyphenyl)tridecyltriphenylphosphonium Bromide (6). Equivalent amounts of 2,2-bis-(4-hydroxyphenyl)tridecyl bromide (4.4746 g, 0.010 mol) and triphenylphosphine (2.631 g, 0.010 mol) were mixed and heated at 100 °C for 8 h under an atmosphere of nitrogen. The melt mixture solidified after the reaction. 2, 2-Bis-(4-hydroxyphenyl)tridecyl triphenylphosphonium bromide **6** was obtained in a pure form as white solid and used without further purification. Melting point: 148 °C. ¹H NMR: 1.14 to 1.46 (16H, m); 1.50 (3H, s); 1.63 (2H, m); 1.93 (2H, m); 3.40 (2H, t); 6.68 (4H, d); 6.93 (4H, d); 7.72 to 7.88 (15H, multiplet).

2.8. Synthesis of 2,2-Bis(4-hydroxyphenyl)tridecyl-(1,2-dimethyl imidazolium) Bromide (7). Equivalent amounts of 2,2-bis-(4-hydroxyphenyl)tridecyl bromide (4.4746 g, 0.010 mol) and 1,2-dimethylimidazole (0.9613 g, 0.010 mol) were mixed and heated at 100 °C for 8 h under an atmosphere of nitrogen. The melt solidified after the reaction. 2, 2-Bis-(4-hydroxyphenyl)tridecyl-(1,2-dimethylimidazolium) bromide **7** was obtained as a transparent yellow solid and used without further purification. Melting point: 78 °C. ¹H NMR 1.14 to 1.48 (16H, m); 1.56 (3H, s); 1.69 (2H, m); 2.01 (2H, m); 2.50 (3H, s); 3.75 (3H, s); 4.03 (2H, t); 6.68 (4H, d); 6.93 (4H, d); 7.42 (2H, m).

2.9. Synthesis of 1-Hexadecyltriphenylphosphonium Bromide (8). Equivalent amounts of hexadecyl bromide (3.05 g, 0.010 mol) and triphenyl phosphine (2.631 g, 0.010 mol) were mixed and heated at 100 °C for 8 h under an atmosphere of nitrogen. The melt solidified after the reaction. Hexadecyl triphenylphosphonium bromide **8** was obtained as white solid

and used without further purification. Yield: 100%. ^1H NMR: 0.88 (3H, t); 1.14 to 1.50 (24H, m); 1.63 (2H, m); 1.93 (2H, m); 3.40 (2H, t); 7.72 to 7.88 (15H, multiplet).

2.10. Synthesis of 1-Hexadecyl-2,3-dimethylimidazolium Bromide (9). Equivalent amounts of hexadecyl bromide (3.05 g, 0.010 mol) and 1,2-dimethylimidazole (0.9613 g, 0.010 mol) were mixed and heated at 100 °C for 8 h under an atmosphere of nitrogen. The melt solidified after the reaction. Hexadecyl-2,3-dimethylimidazolium bromide **9** was obtained as yellow solid and used without further purification. Yield: 100%. ^1H NMR: 0.88 (3H, t); 1.14 to 1.50 (24H, m); 1.65 (2H, m); 2.02 (2H, m); 2.50 (3H, s); 3.75 (3H, s); 4.02 (2H, t); 7.42 (2H, m).

2.11. Synthesis of Organoclays. Na montmorillonite (10 g) with a CEC of 92 meq/100 g was dispersed in water/methanol (300 mL) by stirring with an over head stirrer at room temperature for 2 h. The modifier (11 meq) was dissolved in a methanol/water mixture, and the resulting solution was poured into a dispersion of clay dropwise and stirred for 24 h at 65 °C. The reaction mixture was cooled, centrifuged, and washed several times with distilled water and methanol until all the bromide ions were washed off. The organoclay obtained was freeze-dried under vacuum overnight. The organoclay was obtained as fine, dry powder. The degree of exchange of Na^+ by the organic cation was >99%.

2.12. Synthesis of PC Nanocomposites. Melt polymerization reactions were carried out in a three-neck tubular glass reactor equipped with a solid helical agitator. To remove any sodium from the surface of the glass, the reactor was soaked in 3N HCl for 24 h followed by a soak in deionized water for 24 h. The reactor was then dried in an oven overnight and stored covered until used. The temperature of the reactor was maintained using a salt bath with a proportional–integral–derivative (PID) controller and measured near the reactor and salt bath interface. The pressure over the reactor was controlled by a nitrogen bleed into the vacuum pump downstream of the distillate collection flasks and measured with a digital Pirani gauge. The reactor was charged with bisphenol A (BPA), diphenyl carbonate (DPC), and the organoclay in the desired ratios. The reactor was assembled and sealed, and the atmosphere was exchanged with nitrogen three times. With the final nitrogen exchange, the reactor was brought to near atmospheric pressure and submerged into the molten salt bath, which was at 180 °C. After 5 min, agitation was begun at 100 rpm. Solutions of TMAH (10^{-4} mol/mol of BPA) and NaOH (10^{-6} mol/mol of BPA) were added. After 30 min, the temperature was ramped to 210 °C. The pressure was reduced slowly to 180 mbar at which time phenol started distilling out. After 30 min, the pressure was further reduced to 100 mbar and maintained for 30 min. The temperature was then ramped to 240 °C, and the pressure was lowered to 20 mbar. These conditions were maintained for 30 min. The temperature was then ramped to 260 °C, and the pressure was lowered to 3.5 mbar. These conditions were maintained for 60 min. The temperature was then ramped to the final finishing temperature of 290 °C, and the pressure was reduced to 0.030 mbar. After 4 h, the reactor was removed from the molten salt bath and cooled under vacuum. The nanocomposite was recovered by breaking the glass reactor.

2.13. Separation of PC from the Nanocomposites. PC/nanocomposite (0.300 g) was dissolved in a chloroform/tetrahydrofuran mixture (20/80 v/v, 20 mL), and a 2% solution LiCl in tetrahydrofuran (2 mL) was added slowly under stirring. The stirring continued for 24 h at room temperature. The clay was precipitated due to reverse ion exchange and separated by filtration. The filtrate was poured into methanol to obtain the

precipitate of polymer. The polymer obtained was filtered and dried in vacuo at 60 °C for 6 h and used for further analysis.

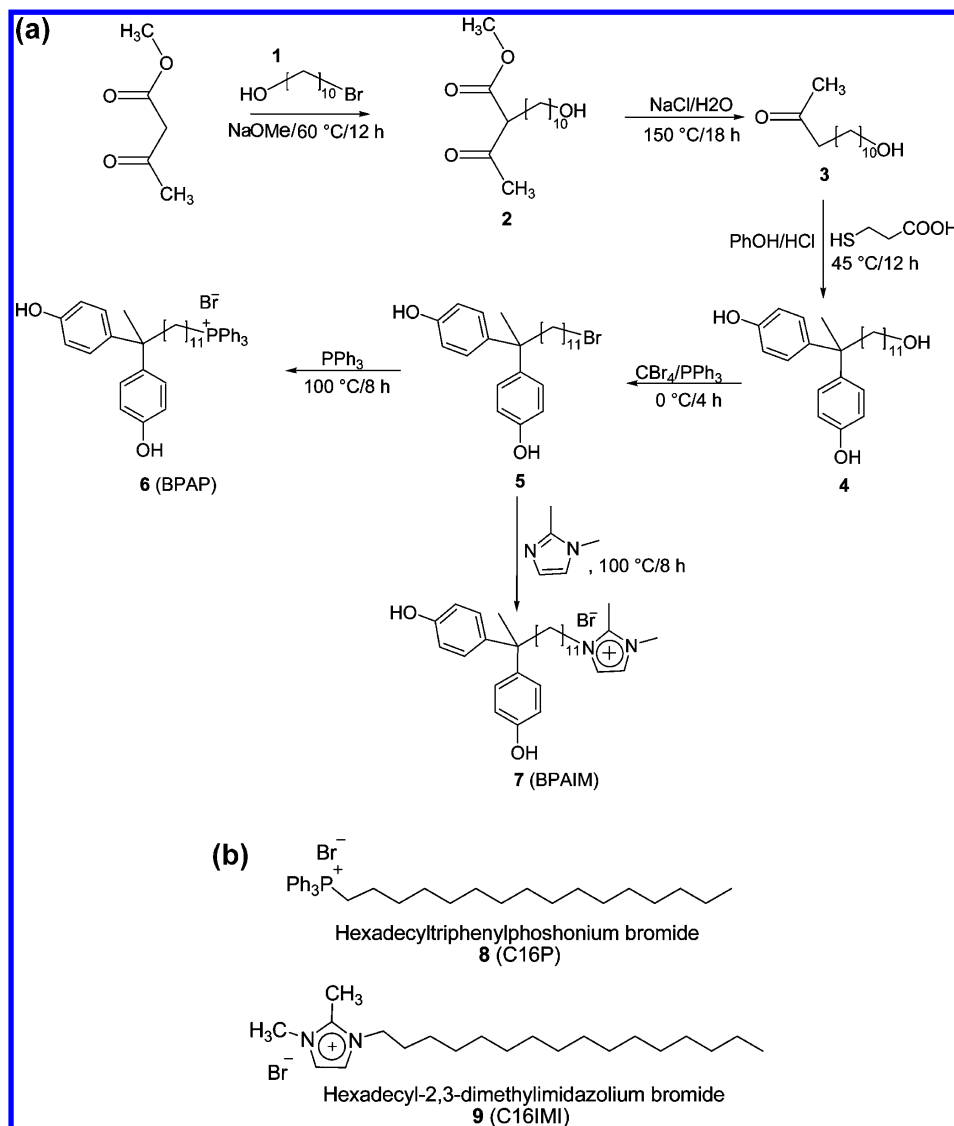
2.14. Analytical Methods. ^1H NMR spectra were recorded in CDCl_3 solution with tetramethylsilane (TMS) as an internal standard using a Bruker DSX300. Molecular weight and molecular weight distributions of polymers were determined using size exclusion chromatography (SEC, *Thermo separation products*) equipped with UV and refractive index (RI) detectors. Linear polystyrene standards were used for calibration of the column. Chloroform filtered through 0.2 μm pore polytetrafluoroethylene (PTFE) membranes was used. The sample concentration was 2 mg/mL, and the injection volume was 50 μL . The thermal properties of the samples were analyzed by a TA Instruments Q10 differential scanning calorimeter. The samples were heated to 280 °C, cooled to 50 °C, and again reheated to 280 °C at a rate of 10 °C/min; the sample weight was about 5 mg, and the T_g was measured from the second heating cycle. Wide angle X-ray diffraction (WAXD) measurements were performed using a Rigaku Dmax 2500 diffractometer fitted with a diffracted beam graphite monochromator. The system consists of a rotating anode generator and wide-angle power goniometer. The generator was operated at 40 kV and 150 mA. The radiation was Ni-filtered Cu K α ; samples were scanned between $2\theta = 2$ and 10°, and the scan speed was 2°/min. A TGA-7 (Perkin-Elmer) thermal analysis system was used to determine the onset of degradation and the organic content in the organoclays. The samples were heated under a flow of nitrogen atmosphere from 50 to 900 °C at a heating rate of 10 °C/min, and the weight loss was recorded. Transmission electron microscopy (TEM) imaging was done using a FEI-Tecnai G² transmission electron microscope operating at an accelerating voltage of 300 kV. Samples for TEM were prepared by sectioning the samples into ultrathin slices (<100 nm) at room temperature using a Leica Ultracut UCT microtome equipped with a diamond knife and then mounted on 200 mesh copper grids. Dynamic mechanical properties of the samples were studied using a Rheometrics dynamic mechanical analyzer, model DMTA IIIIE, that provided a storage modulus against temperature. The scans were carried out in single point cantilever bending mode at a constant heating rate of 2 °C/min and a frequency of 1 Hz from 35 to 170 °C. The samples were cut (with dimension of 25.0 \times 6.0 \times 1.0 mm³) from the sheets obtained by compression molding at 260 °C.

3. Results and Discussion

3.1. Preparation of Organomodifiers for the Clay. Organic modifiers with reactive functional groups were prepared for purposes of this study. The reactive modifier had the following structural features: (a) presence of a functionality which can undergo polycondensation with bisphenol A and diphenyl carbonate; (b) presence of a cationic group that can interact with the negatively charged silicate layer, and (c) an organic cation that is likely to be stable at the temperature of polycondensation. The synthetic approach is shown in Scheme 1a. For purposes of comparison, modifiers such as hexadecyltriphenylphosphonium bromide **8** and hexadecyl-2,3-dimethylimidazolium bromide **9** (Scheme 1b) were also prepared. These modifiers lack the reactive functional groups present in modifiers **6** and **7**.

3.2. Preparation of Organoclays. Four different organoclays were prepared by exchanging Na^+ ion in montmorillonite using 12,12-bis(4-hydroxyphenyl)tridecyltriphenylphosphonium bromide **6**, 12,12-bis(4-hydroxyphenyl)tridecyl-(2,3-dimethylimidazolium) bromide **7**, hexadecyltriphenyl phosphonium bromide **8**, and hexadecyl-2,3-dimethylimidazolium bromide **9**, which

Scheme 1. (a) Preparation of Reactive Modifiers (b) Structure of Hexadecyltriphenylphosphonium Bromide 8 and Hexadecyl-2,3-dimethylimidazolium Bromide 9



are abbreviated as C16P-MMT, C16IM-MMT, BPAP-MMT, and BPAIM-MMT, respectively, using standard exchange reactions reported in the literature.⁴⁰ The interlayer d-spacing for the organo-modified montmorillonite was measured from WAXD (Figure 1) and is shown in Table 1. The intercalation of onium ions in the interlayer gallery is evidenced by increase in d-spacing after organo-modification.

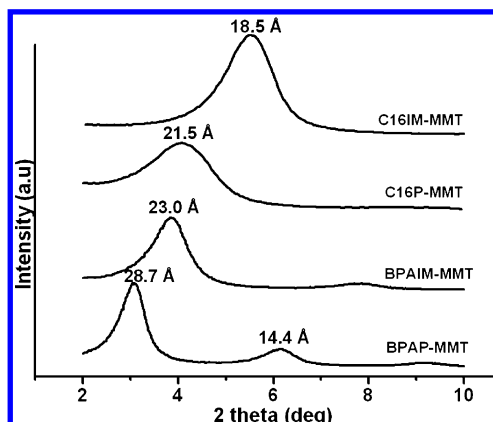


Figure 1. WAXD of various organoclays.

3.3. Thermal Analysis of Organoclays. Figures 2 and 3 show thermal analysis of the organo-modified clays performed using thermogravimetric analysis (TGA). The organoclays degrade in multiple steps. The first onset of degradation for organoclays C16P-MMT and C16IM-MMT is observed at 300 °C, whereas organoclays BPAP-MMT and BPAIM-MMT begin degrading at around 240 °C. The first step in degradation of BPAP-MMT and BPAIM-MMT can be ascribed to the decomposition of the bisphenol group (Scheme 2).^{41,42} However, once the bisphenol is enchain in the polymer, this process of degradation becomes less significant.

In general, the organomodifiers containing imidazolium cations possess a higher onset temperature of degradation compared to phosphonium cations. Therefore, at the outset, it appears that this class of modifiers could be more suitable for the melt polycondensation of BPA with DPC which is generally performed above 250 °C. The weight loss on ignition was obtained from percentage of degradation (obtained from TGA, Figures 2 and 3) of the clays upon heating to 900 °C. The organic content determined experimentally indicates that the exchange of Na⁺ by the organic cation is >99%.

Further, to ascertain that these clays are thermally stable during in situ polycondensation, the TGA of organoclays was

Table 1. TGA and d-Spacing for the Organoclays^a

clay	modifier	onset of degradation (°C)	weight loss on ignition (%)		d-spacing for clay, Å
			theoretical	experimental	
12,12-bis(4-hydroxyphenyl)tridecyl-triphenylphosphonium modified MMT (BPAP-MMT)	6	248	39	40	28.7
12,12-bis(4-hydroxyphenyl)tridecyl(2,3-dimethylimidazolium) modified MMT (BPAIM-MMT)	7	240	31	32	23.0
hexadecyltriphenyl phosphonium modified MMT (C16P-MMT)	8	300	33	33	21.5
hexadecyl-2,3-dimethylimidazolium modified MMT (C16IM-MMT)	9	300	25	26	18.5

^a The unmodified clay had a d-spacing of 12.3 Å.

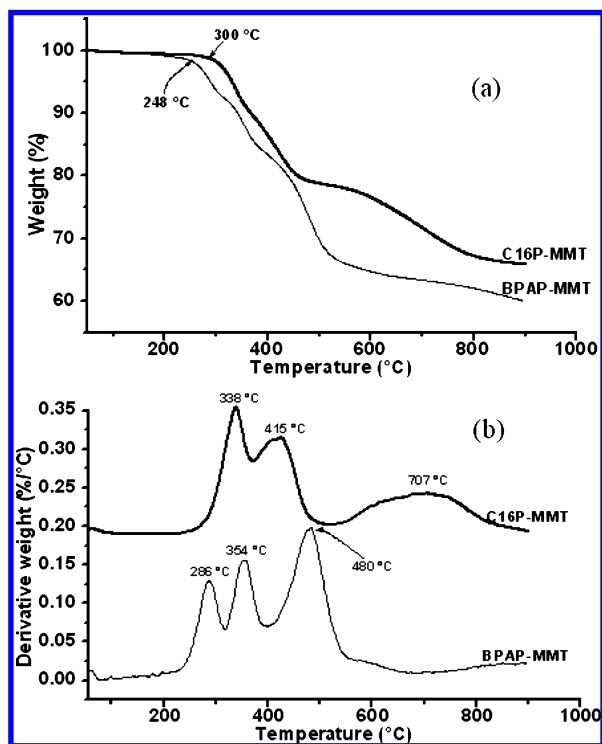


Figure 2. Thermal analysis of organo-modified clays based on phosphonium ions (a) TGA. (b) Derivative thermograms.

performed at the temperature of the polymerization. The TGA of C16P-MMT and C16IM-MMT was performed with a heating program similar to that used for the in situ polycondensation reaction and is shown in Figures 4 and 5, respectively. (First, the sample was heated to 180 °C and held for 15 min. The temperature was raised to 210 °C and held isothermal for 60 min. It was then heated to 240 °C and held isothermal for 30 min. It was heated to 260 °C and held isothermal for 60 min. Finally, it was heated to 290 °C and held for 2 h. The temperature was ramped at a rate of 10 °C/minute whenever it was heated for raising the temperature, and the atmosphere was kept in a flowing nitrogen environment.) The results show that there is no significant weight-loss, confirming that the organoclays based on phosphonium and imidazolium ions are thermally stable and can be conveniently used for preparation of PC/clay nanocomposites via in situ polycondensation.

3.4. Preparation of PC/Clay Nanocomposites Using Phosphonium Cations as Modifiers. PC/clay nanocomposites were prepared via in situ melt polycondensation by mixing the organoclay along with bisphenol A and diphenyl carbonate in the presence NaOH/tetramethylammonium hydroxide as catalyst. PC/clay nanocomposites were also prepared in the absence of catalyst. The final finishing temperature was kept at 290 °C to keep the degradation of the organomodifiers to a minimum. The composition of the monomers, organoclay, and the catalyst taken for the in situ polymerization and the molecular weights of the

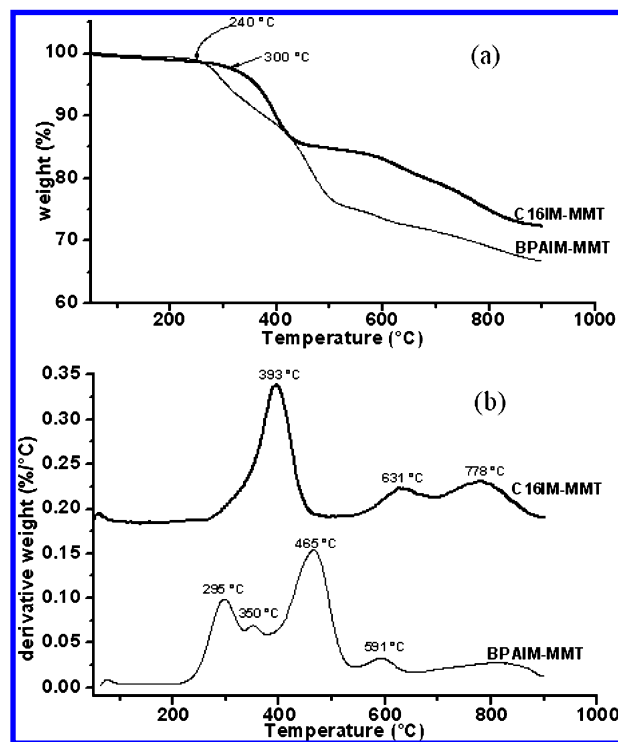
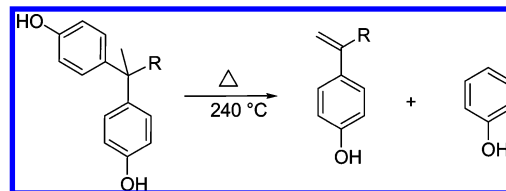


Figure 3. Thermal analysis of organo-modified clays based on imidazolium ions (a) TGA. (b) Derivative thermograms.

Scheme 2. Thermal Decomposition of the Bisphenol Group in the Organomodifiers



polymer obtained are shown in the Table 2. Molecular weights of the polymer in the composites were measured after separating the polymer from the composite by selectively precipitating the clay by reverse ion exchange reaction using LiCl.^{43–45} Bisphenol-A polycarbonates prepared in the presence of a catalyst comprising TMAH and NaOH (pristine PC, Table 2) had a M_n of 22 100, M_w/M_n of 2.31, and T_g of 146 °C. This is similar to what has been previously reported in the literature for PC prepared under similar conditions.^{46–48} Initially, an attempt was made to prepare a nanocomposite using BPAP-MMT in the presence of TMAH/NaOH as a catalyst (BPAP-2, Table 2).

However, under these conditions, a reverse reaction was favored, leading to depolymerization resulting in very low molecular weight PC. Avoiding the use of TMAH/NaOH resulted in better results (BPAP-3, Table 2). Triarylphosphonium salts are reported to catalyze the polycondensation reaction of

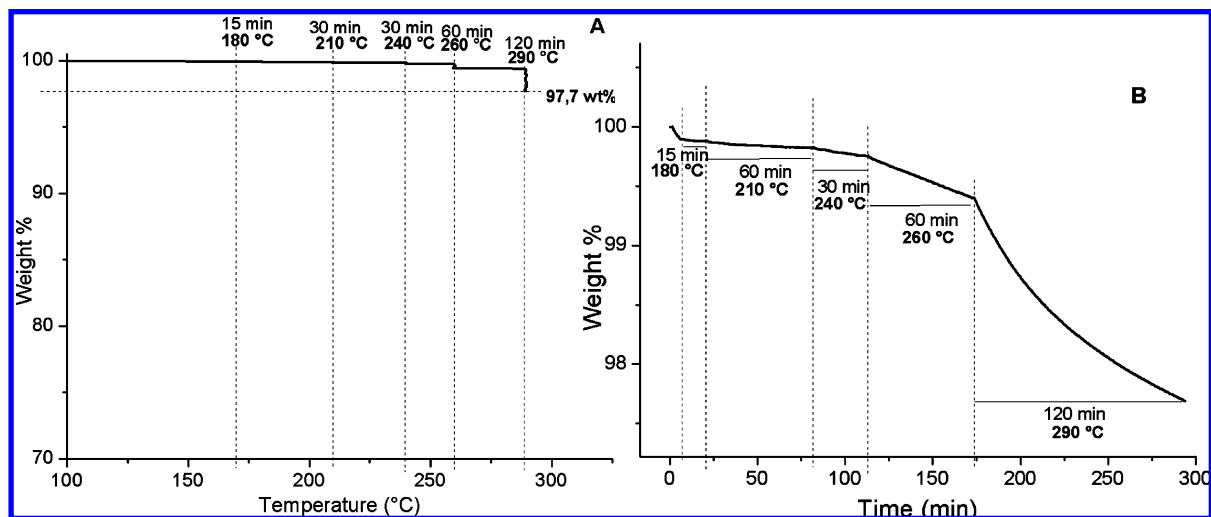


Figure 4. TGA of C16P-MMT with a temperature program similar to the polycondensation reaction. (A) Temperature in x-axis. (B) Time in x-axis.

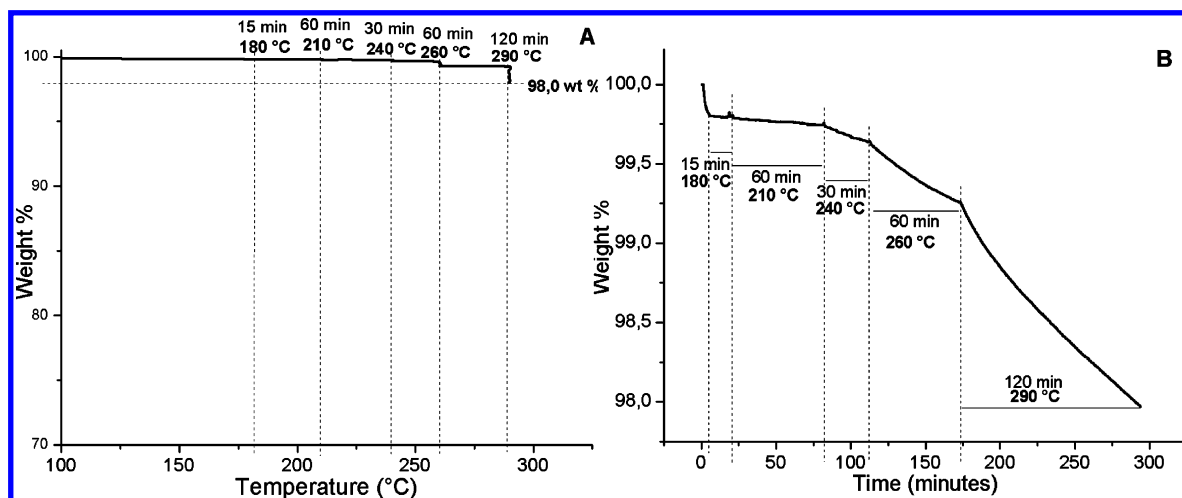


Figure 5. TGA of C16IM-MMT with a temperature program similar to the polycondensation reaction. (A) Temperature in x-axis. (B) Time in x-axis.

Table 2. Melt Polycondensation of Bisphenol A with Diphenyl Carbonate in the Presence Phosphonium Cation-Modified Clay

sample name	organoclay	catalyst ^a	wt % of MMT	mole ratio (DPC/BPA/BPA equivalents in organoclay)	<i>T_g</i> (°C)	polycarbonates ^b		
						<i>T_g</i> (°C)	<i>M_n</i> × 10 ⁻³ ^c	<i>M_w</i> / <i>M_n</i> ^c
pristine PC		TMAH/NaOH		108:100:0	146		22.1	2.31
BPAP-2	BPAP-MMT	TMAH/NaOH	1.8	108:99.6:0.45	124	122	4.4	1.93
BPAP-3	BPAP-MMT		1.8	108:99.6:0.45	145	144	24.5	1.74
BPAP-4	BPAP-MMT		3.6	108:99.1:0.91	144	138	20.7	2.26
BPAP-5	BPAP-MMT		5.3	108:98.6:1.36	145	134	25.0	2.77
C16P-6	C16P-MMT		1.8	108:100:0	141	144	15.0	1.81
C16P-7	C16P-MMT		3.6	108:100:0	143	142	16.5	1.76
C16P-8	C16P-MMT		5.3	108:100:0	142	143	18.8	1.69
BPAIM-9	BPAIM-MMT	TMAH/NaOH	3.6	108:99.1:0.91	128	132	8.3	1.91
BPAIM-10	BPAIM-MMT		3.6	108:99.1:0.91	126	131	8.2	1.94
C16IM-11	C16IM-MMT		3.6	108:100:0	132	138	10.3	2.05

^a TMAH: 10⁻⁴ mmol/mol of BPA; NaOH: 10⁻⁶ mmol/mol of BPA. ^b Obtained from the nanocomposite after ion exchange with LiCl. ^c By GPC in CHCl₃ and calculated with respect to polystyrene standards.

BPA and DPC.⁴⁹ Additionally, residual Na⁺ cation in clay can also act as catalyst for polycondensation. It is well-known that more than optimum quantities of Na⁺ ions can lead to reversal of the polycondensation reaction. Therefore, further studies were conducted in the absence of any externally added catalysts. In all the reactions, the ratio of reactants taken at the beginning of the reaction was BPA/DPC = 1:1.08. An excess of DPC was always taken in the initial feed of the reaction to maintain the stoichiometric balance for the loss of DPC that might occur during the course of the reaction. For preparation of nanocomposites, the amount of BPA taken was corrected for the

bisphenol equivalent present in the organoclay. In general, modifiers containing BPA group led to a higher degree of polymerization (see BPAP-3 and C16P-6, Table 2). The quantity of clay did not influence the degree of polymerization.

3.4.1. Structure of PC Nanocomposites. The WAXD of PC nanocomposites using BPAP-MMT with a varying amount of clay is shown in Figure 6.

The TEM images of PC nanocomposites using BPAP-MMT are shown in Figure 7. In all cases, good dispersion of the clay is observed. The clay layers are well separated, indicative

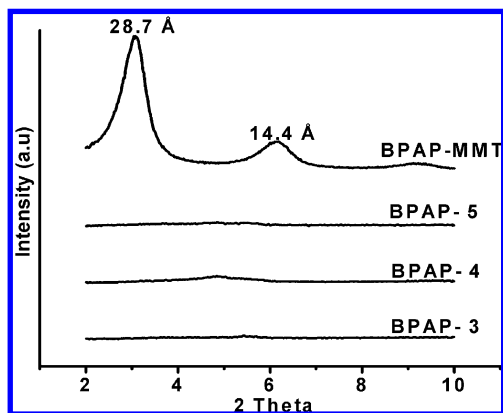


Figure 6. WAXD pattern of BPAP-MMT and the PC nanocomposites (BPAP-3, BPAP-4, and BPAP-5; Table 2).

of well dispersed structures. Thus, WAXD and TEM taken together confirm better delamination of clay layers with organo-modifier 6.

For purposes of comparison, PC nanocomposites were prepared using a clay modified by 1-hexadecyltriphenylphosphonium cation 8. This modifier has no reactive functionality capable of undergoing polycondensation reaction. PC nanocomposites of C16P-MMT show lower d-spacing values (~ 17.8 Å) than the organoclay (21.5 Å) and were independent of the amount of clay (Figure 8; C16P-6, C16P-7, and C16P-8).

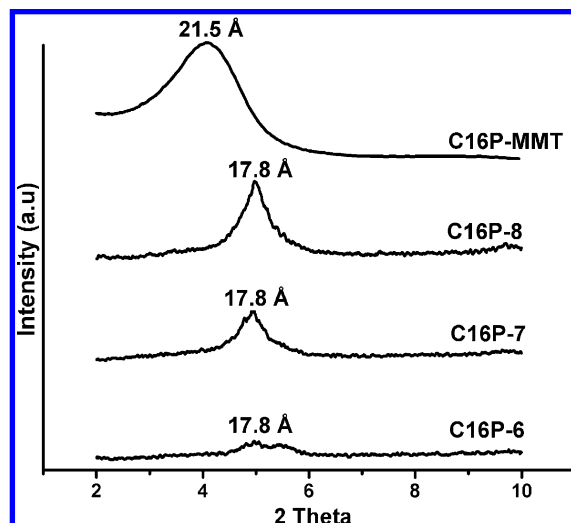


Figure 8. WAXD pattern of C16P-MMT and the PC nanocomposites (C16P-6, C16P-7, and C16P-8; Table 2).

This observation suggests formation of phase separated nanocomposites with a lower d-spacing than the modified clay. This may be due to the deintercalation of modifiers during polymerization, the degradation of modifiers, or the penetration of polymer chains into the organoclay galleries accompanied with deintercalation of modifiers. Figure 9 shows the TEM

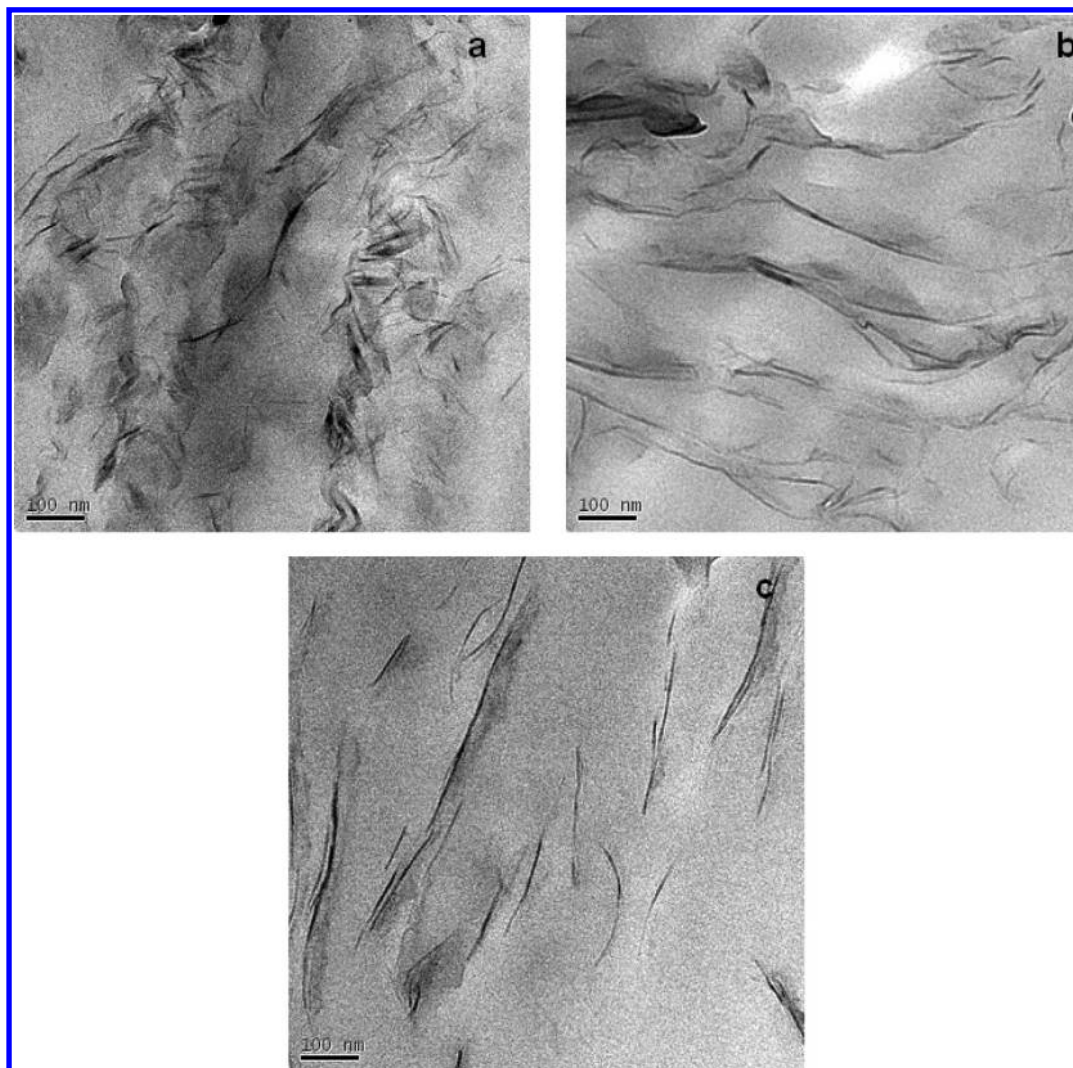


Figure 7. TEM pictures of PC nanocomposites with BPAP-MMT; (a) BPAP-3, (b) BPAP-4, and (c) BPAP-5; Table 2.

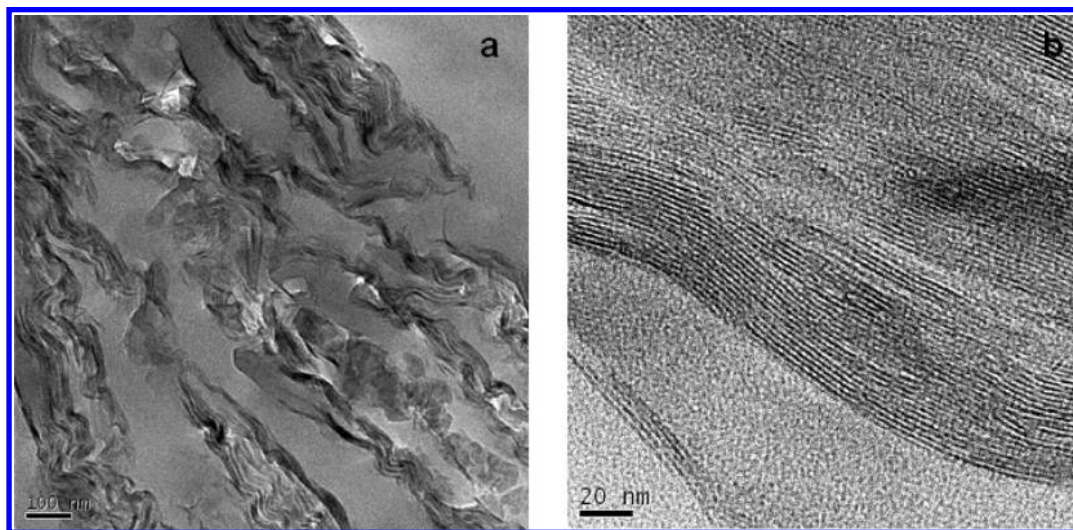


Figure 9. TEM pictures of PC Nanocomposite with C16P-MMT (C16P-7, Table 2) at different magnifications.

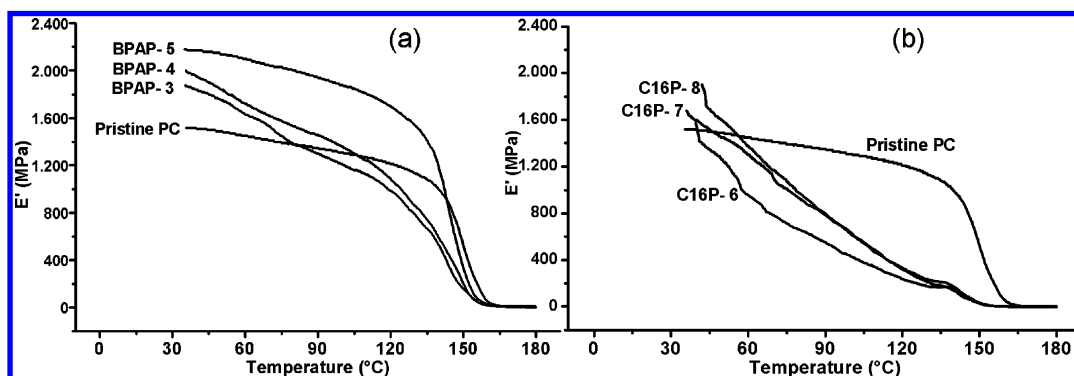


Figure 10. Storage modulus (E') of PC nanocomposites (a) with BPAP-MMT and (b) with C16P-MMT.

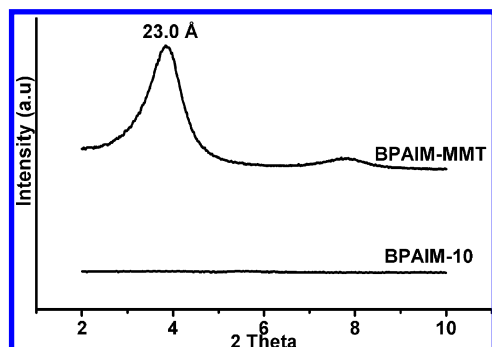


Figure 11. WAXD pattern of pristine BPAIM-MMT and the PC nanocomposite (BPAIM-10; Table 2).

image of the C16P-MMT nanocomposites with 3.6% of clay content at different magnifications. The nanocomposites show intercalated structures. At higher magnification (Figure 9b), the silicate layers are shown to be arranged in an ordered array parallel to each other with an interlayer distance of 18 Å, comparable to that obtained from WAXD.

3.4.2. Glass Transition Temperatures. The effect of organo-modifiers on the T_g of nanocomposites was examined. For purposes of comparison, the PC was separated from the corresponding nanocomposites using a reverse ion exchange reaction and the T_g of the isolated PC was determined. The results are shown in Table 2. It is observed that the T_g of the polymer separated from the nanocomposites based on BPAP-MMT is lower than that of the corresponding nanocomposites, especially at higher clay content. The lower T_g for the separated

polymer may be attributed to the presence of a C_{11} alkyl group in the polymer. On the basis of the assumption that the entire modifier became enchain, the mole % modifier with a C_{11} side chain in the PC is expected to be 0.45, 0.91, and 1.35 mol %, respectively, for polymer at BPAP-3, BPAP-4, and BPAP-5. The slightly lower T_g for these nanocomposite extracts may be attributed to the plastisizer effect of the modifiers.

On the other hand, no significant difference was observed in T_g for the matrix polymer and nanocomposites based on C16P-MMT since, in this case, the C16 alkyl group cannot become part of the polymer. The T_g of the BPAP-MMT nanocomposites was greater in general than that of the C16P-MMT nanocomposites which is consistent with grafting to the surface in the case of BPAP-MMT, thus lowering chain mobility.

3.4.3. Dynamic Mechanical Behavior. Dynamic mechanical properties of PC nanocomposites using an organoclay modified with phosphonium cations were measured. Figure 10a,b shows the temperature dependence of storage modulus (E') of nanocomposites based on BPAP-MMT and C16P-MMT, respectively.

It is observed that, at 35 °C, the nanocomposites generally exhibit higher storage modulus (E') than the pristine polymer and increase linearly with the clay content. The increase in storage modulus (E') is much higher for exfoliated nanocomposites obtained using BPAP-MMT compared to the nanocomposites obtained using C16P-MMT. With an increase in temperature, the storage modulus progressively decreases prior to T_g (α -relaxation). This rate of change in storage modulus is relatively faster in the case of nanocomposites based on C16P-MMT compared to nanocomposites based on BPAP-MMT. The

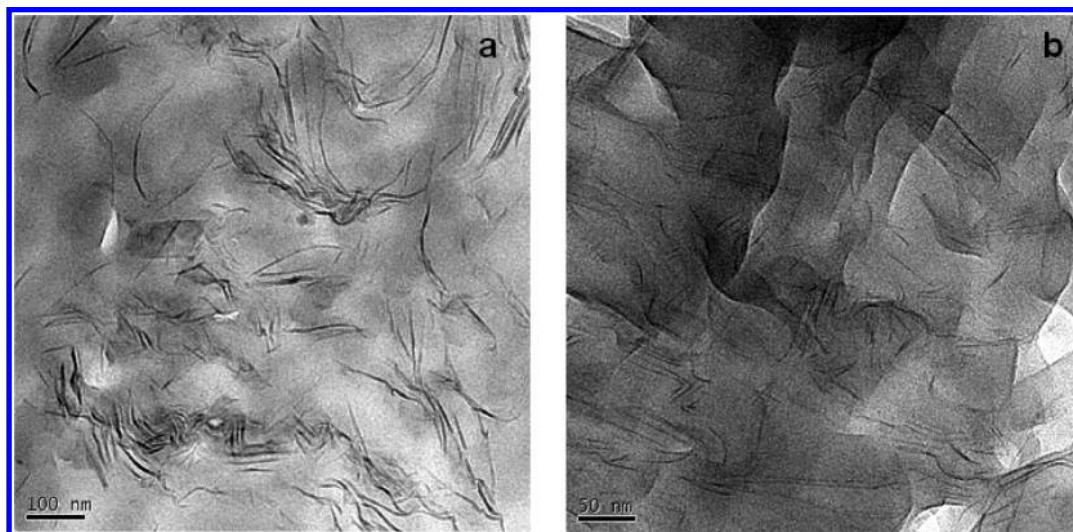


Figure 12. TEM pictures of PC nanocomposites with BPAIM-MMT (BPAIM-10; Table 2) at different magnifications.

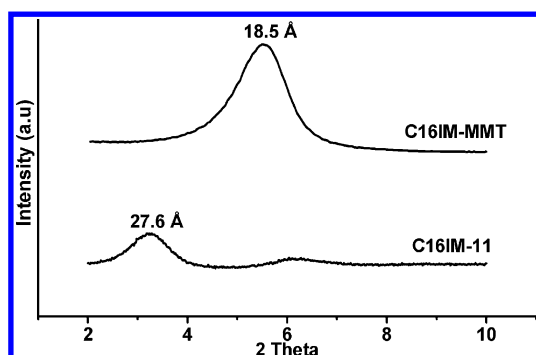


Figure 13. WAXD pattern of pristine C16IM-MMT and the PC nanocomposite (C16IM-11; Table 2).

C16P-MMT nanocomposites do not exhibit a plateau, indicating interference with entanglement. Faster relaxation can be attributed due to the enhanced mobility of confined polymer chains at the interface of polymer–silicate layers, as has been reported by various groups.^{50–55} Such relaxations are known to be limited to the nanoregime. Poor interfacial interactions may be responsible for the faster relaxation behavior of the agglomerated nanocomposites based on C16P-MMT. This observation is in good agreement with the earlier reports.^{56,57} The relatively

slower relaxation behavior of the exfoliated nanocomposites is attributed to the restricted mobility of polymer chains anchored on the clay surface.^{58,59}

3.4.4. Color of the Nanocomposites. Nanocomposites prepared via in situ polycondensation using organoclays which are modified using phosphonium cations are found to be dark brown in color. Thus, use of a quaternary phosphonium modifier, whose temperature of degradation is slightly higher than the polycondensation temperature, did not result in an expectant improvement in color. The appearance of a dark coloration in PC is indicative of undesirable side reactions leading to intensely absorbing chromophores.^{12,60} Such reactions are known to be catalyzed by monovalent and divalent alkaline earths and transition metal ions. The clays used in the study were found to contain substantial amounts of Ca^{2+} (1.03 wt %) and Fe^{3+} (3.24 wt %). Apparently, this causes the discoloration of PC. Therefore, it may be suggested that use of a clay or synthetic clay devoid of Fe and Ca may be useful in improving the color of PC nanocomposites.

3.5. Preparation of PC/Clay Nanocomposites Using Imidazolium Cations as Modifiers. PC/clay nanocomposites were prepared using imidazolium cation modified organoclays. The T_g and molecular weight informations are given in Table 2. All imidazolium based nanocomposites showed T_g 's well under the

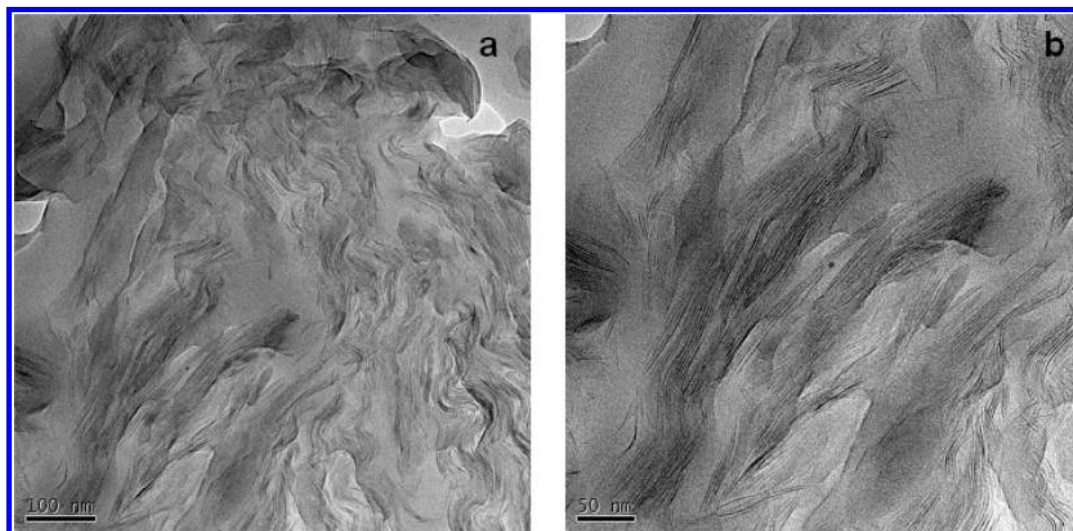


Figure 14. TEM pictures of PC nanocomposites with C16IM-MMT (C16IM-11; Table 2) at different magnifications.

control T_g for a PC of 146 °C shown in Table 2. The results are indicative of decomposition of the modifier during polymerization, resulting in free imidazole formation. Imidazoles, which are bases, in high concentration are known to be efficient depolymerization agents for PC.²⁹ This is consistent with enhancement of the depolymerization reaction and resultant low molecular weights for PC (Table 2).

3.5.1. Structure of PC Nanocomposites. Figure 11 shows the WAXD of PC nanocomposites prepared using the organoclay, BPAIM-MMT (BPAIM-10, Table 2). The peak for the pristine organoclay at 23.0 Å completely disappeared in the nanocomposites. TEM of PC nanocomposites using BPAIM-MMT (BPAIM-10, Table 2) at different magnifications are shown in Figure 12. The clay layers are well separated and thoroughly dispersed in the polymer matrix indicative of exfoliated structures. Thus, WAXD and TEM taken together confirm formation of predominantly exfoliated structures in PC/clay nanocomposites with organo-modifier 7.

For purposes of comparison, PC nanocomposites were prepared using clay modified by a 1-hexadecyl-2,3-dimethylimidazolium cation. This modifier has no reactive functionality capable of undergoing polycondensation reaction. Figure 13 shows the WAXD of nanocomposites prepared using C16IM-MMT (C16IM-11, Table 2). The peak for the organoclay at 18.5 Å has shifted to 27.6 Å, indicating the formation of intercalated structures.

TEM of PC nanocomposites based on C16IM-MMT (C16IM-11, Table 2) at different magnifications are shown in Figure 14. The silicate layers are shown to be arranged parallel to each other in stacks with an interlayer distance of 28 Å, comparable to that obtained from WAXD which further confirms the formation of intercalated structures.

4. Summary and Conclusions

PC/clay nanocomposites were prepared via in situ intercalative melt polycondensation using organoclays modified with quaternary phosphonium and imidazolium cation based modifiers with and without reactive functionalities. In general, exfoliated PC/clay nanocomposites were obtained using an organoclay which contained a reactive bisphenol group in the modifier, whereas only intercalated or phase separated structures were obtained with organoclays which were modified using compounds having no reactive functionality. Organoclays modified using phosphonium cations presumably act as a catalyst for polycondensation and produce high molecular weight PC even in the absence of any additional base catalysts. Organoclays which are modified using imidazolium cations resulted in low molecular weight polymers, indicative of competitive depolymerization. This was attributed to the formation of free imidazole base during polymerization. Though the nanocomposites prepared using imidazolium based modifiers show evidence of depolymerization, when they possess a bisphenol unit, it resulted in predominantly exfoliated structures, which could represent an important technique for production of a masterbatch for later melt extrusion. Well dispersed PC/clay nanocomposites obtained using organoclays modified with phosphonium ions containing a reactive bisphenol group show slightly higher glass transition temperature than PC separated from the clay. The increase in storage modulus is significantly improved for the BPAP-MMT nanocomposites versus the C16P-MMT nanocomposites. This effect dramatically supports significant dispersion and even exfoliation of the organoclay particles in the case of BPAP-MMT. Use of organomodifiers which had higher thermal stability than quaternary ammonium based modifiers did not

cause any improvement in the color in PC nanocomposites. All PC/clay nanocomposites obtained in this study were dark brown in color. Formation of such color in PC is attributed to complex degradation reactions promoted by excess basic compounds or multivalent metal ions. The clays used in the present study had a significant level of Fe^{3+} . Thus, it is demonstrated that well dispersed PC/clay nanocomposites can be prepared via in situ melt polymerization using organoclays which are modified using thermally phosphonium cations containing reactive bisphenol functionality. Interaction between the polymer chains and the clay layers is enhanced as the polymer chains are anchored on to the clay surface through electrostatic forces. Such nanocomposites are expected to have superior thermal, mechanical, and barrier properties. However, the color of the nanocomposites still needs considerable improvements if such nanocomposites have to find significant practical applications. It is suggested that use of a clay or synthetic clay devoid of Fe and Ca may improve the color in PC nanocomposites.

Acknowledgment

SRM is grateful to Council of Scientific and Industrial Research, India (CSIR) for Research Fellowship.

Literature Cited

- (1) LeGrand, D. G. Mechanical properties of polycarbonates. In *Handbook of Polycarbonate Science and Technology*; LeGrand, D. G., Bendler, J. T., Eds.; Marcel Dekker, Inc.: New York, 2000, p 107.
- (2) Friessell, W. J. In *Encyclopedia of Polymer Science and Technology*; Bikales, N. M., Ed.; John Wiley and Sons Inc: New York, 1967; Vol. 6, p 740.
- (3) Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. Synthesis of nylon 6-clay hybrid. *J. Mater. Res.* **1993**, *8*, 1179.
- (4) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. Mechanical properties of nylon 6-clay hybrid. *J. Mater. Res.* **1993**, *8*, 1185.
- (5) Pinnavaia, T. J.; Beall, G. W., Eds. *Polymer-Clay Nanocomposites*; Wiley Series in Polymer Science; John Wiley & Sons Ltd: Chichester, England, 2000.
- (6) Giannelis, E. P. Polymer-layered silicate nanocomposites. *Adv. Mater.* **1996**, *8*, 29.
- (7) Carrado, K. A. Synthetic organo- and polymer-clays: preparation, characterization, and materials applications. *Appl. Clay Sci.* **2000**, *17*, 1.
- (8) Porter, D.; Metcalfe, E.; Thomas, M. J. K. Nanocomposite fire retardants—a review. *Fire Mater.* **2000**, *24*, 45.
- (9) Ray, S. S.; Okamoto, M. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Prog. Polym. Sci.* **2003**, *28*, 1539.
- (10) Huang, X.; Lewis, S.; Brittain, W. J.; Vaia, R. A. Synthesis of polycarbonate-layered silicate nanocomposites via cyclic oligomers. *Macromolecules* **2000**, *33*, 2000.
- (11) Yoon, P. J.; Hunter, D. L.; Paul, D. R. Polycarbonate nanocomposites. Part 1. Effect of organoclay structure on morphology and properties. *Polymer* **2003**, *44*, 5323.
- (12) Yoon, P. J.; Hunter, D. L.; Paul, D. R. Polycarbonate nanocomposites: Part 2. Degradation and color formation. *Polymer* **2003**, *44*, 5341.
- (13) Gonzalez, I.; Eguiazabal, J. I.; Nazabal, J. New clay-reinforced nanocomposites based on a polycarbonate/polycaprolactone blend. *Polym. Eng. Sci.* **2006**, *46*, 864.
- (14) Ray, S. S.; Bousmina, M.; Maazaouz, A. Morphology and properties of organoclay modified polycarbonate/poly(methyl methacrylate) blend. *Polym. Eng. Sci.* **2006**, *46*, 1121.
- (15) Wang, S.; Hu, Y.; Wang, Z.; Yong, T.; Chen, Z.; Fan, W. Synthesis and characterization of polycarbonate/ABS/montmorillonite nanocomposites. *Polym. Degrad. Stab.* **2003**, *80*, 157.
- (16) Zong, R.; Hu, Y.; Wang, S.; Song, L. Thermogravimetric evaluation of PC/ABS/montmorillonite nanocomposite. *Polym. Degrad. Stab.* **2004**, *83*, 423.
- (17) Zong, R.; Hu, Y.; Liu, N.; Wang, S.; Liao, G. Evaluation of the thermal degradation of PC/ABS/montmorillonite nanocomposites. *Polym. Adv. Technol.* **2005**, *16*, 725.

- (18) Wang, S.; Hu, Y.; Song, L.; Liu, J.; Chen, Z.; Fan, W. Study on the dynamic self-organization of montmorillonite in two phases. *J. Appl. Polym. Sci.* **2004**, *91*, 1457.
- (19) Wu, D.; Wu, L.; Zhang, M.; Wu, L. Effect of epoxy resin on rheology of polycarbonate/clay nanocomposites. *Eur. Polym. J.* **2007**, *43*, 1635.
- (20) Guduri, B. R.; Luyt, A. S. Structure and mechanical properties of polycarbonate modified clay nanocomposites. *J. Nanosci. Nanotechnol.* **2008**, *8*, 1880.
- (21) Mitsunaga, M.; Ito, Y.; Ray, S. S.; Okamoto, M.; Hironaka, K. Intercalated polycarbonate/clay nanocomposites: Nanostructure control and foam processing. *Macromol. Mater. Eng.* **2003**, *288*, 543.
- (22) Ito, Y.; Yamashita, M.; Okamoto, M. Foam processing and cellular structure of polycarbonate-based nanocomposites. *Macromol. Mater. Eng.* **2006**, *291*, 773.
- (23) Hsieh, A. J.; Moy, P.; Beyer, F. L.; Madison, P.; Napadensky, E.; Ren, J.; Krishnamoorti, R. Mechanical response and rheological properties of polycarbonate layered-silicate nanocomposites. *Polym. Eng. Sci.* **2004**, *44*, 825.
- (24) Carrion, F.-J.; Arribas, A.; Bermudez, M.-D.; Guillamon, A. Physical and tribological properties of a new polycarbonate-organoclay nanocomposite. *Eur. Polym. J.* **2008**, *44*, 968.
- (25) Hu, X.; Lesser, A. J. Enhanced crystallization of bisphenol-A polycarbonate by nano-scale clays in the presence of supercritical carbon dioxide. *Polymer* **2004**, *45*, 2333.
- (26) Lee, K. M.; Han, C. D. Effect of hydrogen bonding on the rheology of polycarbonate/organoclay nanocomposites. *Polymer* **2003**, *44*, 4573.
- (27) Yoo, Y.; Choi, K.-Y.; Lee, J. H. Polycarbonate/montmorillonite nanocomposites prepared by microwave-aided solid state polymerization. *Macromol. Chem. Phys.* **2004**, *205*, 1863.
- (28) Xie, W.; Pan, W.-P.; Hunter, D.; Vaia, R. Thermal degradation chemistry of alkyl quaternary ammonium montmorillonites. *Chem. Mater.* **2001**, *13*, 2979.
- (29) Foldi, V. S.; Campbell, T. W. Preparation of copoly(carbonate/urethanes) from polycarbonates. *J. Polym. Sci.* **1962**, *56*, 1.
- (30) Xie, W.; Xie, R. C.; Pan, W. P.; Hunter, D.; Koene, B.; Tan, L. S.; Vaia, R. Thermal stability of quaternary phosphonium modified montmorillonites. *Chem. Mater.* **2002**, *14*, 4837.
- (31) Gilman, J. W.; Awad, W. H.; Davis, R. D.; Shields, J.; Harris, R. H., Jr.; Davis, C.; Morgan, A. B.; Sutto, T. E.; Callahan, J.; Trulove, P. C.; DeLong, H. C. Polymer/layered silicate nanocomposites from thermally stable trialkylimidazolium-treated montmorillonite. *Chem. Mater.* **2002**, *14*, 3776.
- (32) Awad, W. H.; Gilman, J. W.; Nyden, M.; Harris, R. H., Jr.; Sutto, T. E.; Callahan, J.; Trulove, P. C.; DeLong, H. C.; Fox, D. M. Thermal degradation studies of alkyl-imidazolium salts and their application in nanocomposites. *Thermochim. Acta* **2004**, *40*, 3.
- (33) Severe, G.; Hsieh, A. J.; Koene, B. E. Effect of layered silicates on thermal characteristics of polycarbonate nanocomposites. *ANTEC 2000* **2000**, *2*, 1523.
- (34) Imai, Y.; Nishimura, S.; Abe, E.; Tateyama, H.; Abiko, A.; Yamaguchi, A.; Taguchi, H. High-modulus poly(ethylene terephthalate)/expandable fluorine mica nanocomposites with a novel reactive compatibilizer. *Chem. Mater.* **2002**, *14*, 477.
- (35) Messersmith, P. B.; Giannelis, E. P. Polymer-layered silicate nanocomposites: in situ intercalative polymerization of ϵ -caprolactone in layered silicates. *Chem. Mater.* **1993**, *5*, 1064.
- (36) Weimer, M. W.; Chen, H.; Giannelis, E. P.; Sugah, D. Y. Direct synthesis of dispersed nanocomposites by in situ living free radical polymerization using a silicate-anchored initiator. *J. Am. Chem. Soc.* **1999**, *121*, 1615.
- (37) Tyan, H.-L.; Liu, Y.-C.; Wei, K.-H. Thermally and mechanically enhanced clay/polyimide nanocomposite via reactive organoclay. *Chem. Mater.* **1999**, *11*, 1942.
- (38) Leu, C.-M.; Wu, Z.-W.; Wei, K.-H. Synthesis and properties of covalently bonded layered silicates/polyimide (BTDA-ODA) nanocomposites. *Chem. Mater.* **2002**, *14*, 3016.
- (39) Zeng, C.; Lee, L. J. Poly(methyl methacrylate) and polystyrene/clay nanocomposites prepared by in situ polymerization. *Macromolecules* **2001**, *34*, 4098.
- (40) Vaia, R. A.; Teukolsky, R. K.; Giannelis, E. P. Interlayer structure and molecular environment of alkylammonium layered silicates. *Chem. Mater.* **1994**, *6*, 1017.
- (41) Schnell, H.; Krimm, H. Formation and cleavage of dihydroxydiarylmethane derivatives. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 373.
- (42) Dai, S. H.; Lin, C. Y.; Rao, D. V.; Stuber, F. A.; Carleton, P. S.; Ulrich, H. Selective indirect oxidation of phenol to hydroquinone and catechol. *J. Org. Chem.* **1985**, *50*, 1722.
- (43) Messersmith, P. B.; Giannelis, E. P. Synthesis and barrier properties of poly(ϵ -caprolactone)-layered silicate nanocomposites. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1047.
- (44) Lepoittevin, B.; Pantoustier, N.; Devalckenaere, M.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. Poly(ϵ -caprolactone)/clay nanocomposites by in situ intercalative polymerization catalyzed by dibutyltin dimethoxide. *Macromolecules* **2002**, *35*, 8385.
- (45) Kubies, D.; Pantoustier, N.; Dubois, P.; Rulmont, A.; Jerome, R. Controlled ring-opening polymerization of ϵ -caprolactone in the presence of layered silicates and formation of nanocomposites. *Macromolecules* **2002**, *35*, 3318.
- (46) McCloskey, P. J.; Burnell, T. B.; Smigelski, P. M., Jr. (General Electric Company). U. S. Patent 6,228,973, 2001.
- (47) Lemmon, J. P.; McCloskey, P. J.; Siclovian, O. P. (General Electric Company). U. S. Patent 6,323,304, 2001.
- (48) Lemmon, J. P.; McCloskey, P. J.; Siclovian, O. P. (General Electric Company). U. S. Patent 6,376,640, 2001.
- (49) King, J. A., Jr.; McCloskey, P. J. (General Electric Company). U. S. Patent 6,376,640, 1995.
- (50) Barut, G.; Pissis, P.; Pelster, R.; Nimtz, G. Glass Transition in Liquids: Two versus Three-Dimensional Confinement. *Phys. Rev. Lett.* **1998**, *80*, 3543.
- (51) Schonhals, A.; Stauga, R. Broadband dielectric study of anomalous diffusion in a poly(propylene glycol) melt confined to nanopores. *J. Chem. Phys.* **1998**, *112*, 5130.
- (52) Schonhals, A.; Stauga, R. Dielectric normal mode relaxation of poly(propylene glycol) melts in confining geometries. *J. Non-Cryst. Solids* **1998**, *235–237*, 450.
- (53) Huwe, A.; Kremer, F.; Behrens, P.; Schwieger, W. Molecular Dynamics in Confining Space: From the Single Molecule to the Liquid State. *Phys. Rev. Lett.* **1999**, *82*, 2338.
- (54) Baschnagel, J.; Mischler, C.; Binder, K. Dynamics of confined polymer melts: Recent Monte Carlo simulation results. *J. Phys. IV* **2000**, *10*, 7–9.
- (55) Huwe, A.; Kremer, F.; Hartmann, L.; Kratzmüller, Th.; Braun, H. G.; Kärger, J.; Behrens, P.; Schwieger, W.; Ihlein, G.; Weib ö; Schüth, F. Molecular dynamics in confining geometries. *J. Phys. IV* **2000**, *10*, 7–59.
- (56) Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R. Interface and chain confinement effects on the glass transition temperature of thin polymer films. *Phys. Rev. E* **1997**, *56*, 5705.
- (57) Dalnoki-Veress, K.; Forrest, J. A.; Murray, C.; Gigault, C.; Dutcher, J. R. Molecular weight dependence of reductions in the glass transition temperature of thin, freely standing polymer films. *Phys. Rev. E* **2001**, *63*, 31801.
- (58) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. Interface and surface effects on the glass-transition temperature in thin polymer films. *Faraday Discuss.* **1994**, *98*, 219.
- (59) Keddie, J. L.; Jones, R. A. L. Glass transition behavior in ultrathin polystyrene films. *Isr. J. Chem.* **1995**, *35*, 21.
- (60) Factor, A. Degradation of bisphenol A polycarbonate by light and γ -ray irradiation. In *Handbook of Polycarbonate Science and Technology*; LeGrand, D. G., Bendler, J. T., Eds.; Marcel Dekker, Inc.: New York, 2000; p 267.

Received for review October 7, 2009

Revised manuscript received January 7, 2010

Accepted January 11, 2010

IE9015649