Notes

Poly(methyl methacrylate)-*graft*-poly[bis(trifluoroethoxy)phosphazene] Copolymers: Synthesis, Characterization, and Effects of Polyphosphazene Incorporation

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Introduction

One of the most important characteristics of the polyphosphazene system is the ease with which different pendent groups can be linked to the phosphorus−nitrogen backbone.[1] Properties such as hydrophobicity,[2] hydrophilicity,[3] liquid crystallinity,[4] NLO activity,[5] photochromic responsiveness,[6] and high or low refractive indices[7] can be introduced into a polyphosphazene by covalently binding an appropriate side group to the phosphorus atoms in the backbone. The bulk properties of a polyphosphazene can also be tailored by linking two or more different side groups to the same polymer chain. Moreover, the phosphorus−nitrogen skeleton imparts fire resistance to many polyphosphazene systems.[8]

An objective of our current research is to use these attributes to improve the properties of classical organic polymers. A number of examples that illustrate the principles involved have been reported by our research group.[9−13] One approach involves the covalent linkage of cyclotriphosphazene pendent groups to organic polymer chains.[9] Another incorporates cyclotriphosphazene molecules directly into the backbone of hydrocarbon polymers.[10] A third strategy involves the synthesis of hybrid block and graft copolymers of polyphosphazenes with organic polymers.[11−13]

In the work described here, graft copolymers of poly(methyl methacrylate) (PMMA) with linear polyphosphazene side-chain grafts have been synthesized. The methodology involves the use a living, cationic polymerization to first synthesize well-defined styryl-telechelic polyphosphazenes that bear appropriate side groups.[14−16] The terminal styrene unit is then copolymerized with methyl methacrylate to yield a graft copolymer. A previous communication from our lab reported the synthesis of polystyrene-*graft*-poly[bis(trifluoroethoxy)phosphazene] copolymers as the first graft copolymers of that structure, using styryl-telechelic polyphosphazenes as a building block. This work demonstrates the utility of styryl-telechelic polyphosphazenes for copolymerization with unsaturated monomers other than styrene and examines the effect of increasing polyphosphazene incorporation on the bulk properties of the copolymer system.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide and 95% sodium hydride were obtained from Aldrich and were used without further purification. Phosphorus pentachloride (Aldrich) was purified by sublimation under vacuum before use. 2,2,2-Trifluoroethanol (Aldrich) and methyl methacrylate (Aldrich) were dried over calcium hydride (CaH_2) and distilled under reduced pressure prior to use. Azobis(isobutyronitrile) (AIBN) was obtained from Aldrich and was recrystallized from methanol before use. The phosphoranimines $Cl_3P{=}NSiMe_3$, $Br(CF_3CH_2O)_2P{=}NSiMe_3$, and $(CF_3CH_2O)_3P{=}NSiMe_3$ were synthesized according to literature procedures.[17−19] Tetrahydrofuran (THF) and hexanes were obtained from EM Science and were distilled into the reaction flask from sodium benzophenone ketyl under a dry argon atmosphere. Dichloromethane (CH_2Cl_2) was obtained from EM Science, dried over $CaSO_4$, and distilled into the reaction flask from CaH_2 under a dry argon atmosphere.

All glassware was flame-dried under vacuum before use. Reactions were carried out using standard Schlenk techniques or in an inert atmosphere glovebox (MBraun) under a dry nitrogen atmosphere.

Instrumentation. ^1H and ^{31}P NMR spectra were obtained using a Bruker AMX-360 NMR spectrometer, operated at 360 and 146 MHz, respectively. ^1H NMR spectra were referenced to solvent signals while ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. All chemical shifts are reported in ppm. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 μm mixed MXL and linear (2) analytical columns, and were calibrated against polystyrene standards (Polysciences). The samples were eluted at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (EM Science).

Static contact angles of water droplets on films of graft copolymers were measured using a Rame-Hart, Inc., model 100-00 contact angle goniometer. Films were cast from 25 wt % solutions onto glass substrates and were dried at 40 °C under reduced pressure before measurements were taken.

Synthesis of $CH_2{=}CH{-}C_6H_4{-}NH{-}P(OCH_2CF_3)_2{=}NSiMe_3$ (2). The phosphoranimine $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (10.0 g, 25.3 mmol) was dissolved in 150 mL of dry THF. Triethylamine (10.2 g, 101 mmol) was added, and the solution was cooled to −78 °C in a dry ice/2-propanol bath. To this solution, 4-vinylaniline (3.01 g, 25.3 mmol) was added slowly over 30 min, after which time the reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. Salts were removed by filtration through Celite under an inert atmosphere, and all volatiles were removed under reduced pressure. The resultant oil was distilled under high vacuum (74 °C, 5 mmHg) to yield a clear, pale yellow oil (72% yield). ^1H NMR ($CDCl_3$): $\delta = 7.41$ (d, 2H), 7.06 (d, 2H), 6.75 (m, 1H), 5.77 (d, 1H), 5.28 (d, 1H), 4.30 (m, 4H), 0.04 (d, 9H). ^{31}P NMR ($CDCl_3$): $\delta = -16.72$ (s).

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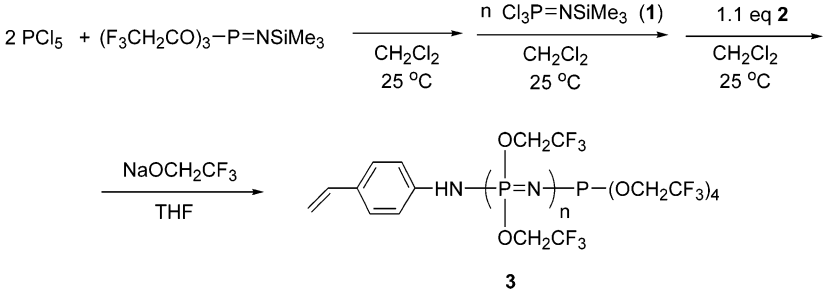
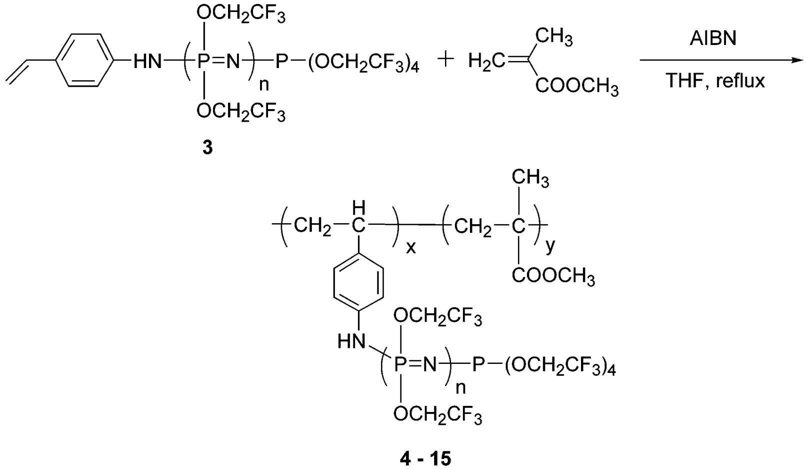
Scheme 1. Synthesis of a Styryl-Telechelic Poly[bis(trifluoroethoxy)phosphazene] Prepolymer



Scheme 2. Synthesis of a Poly(methyl methacrylate)-*graft*-Poly[bis(trifluoroethoxy)phosphazene] Copolymer under Free Radical Conditions[a]



[a] *x* and *y* indicate a statistical distribution and not a blocky nature of the backbone.

General Synthesis of a Styryl-Telechelic Poly[bis(trifluoroethoxy)phosphazene] Prepolymer (3). Phosphorus pentachloride (104.0 mg, 0.5 mmol, 2 equiv) was dissolved in 50 mL of CH_2Cl_2 during 1 h at room temperature. To this solution was added 104.0 mg (0.25 mmol, 1 equiv) of the phosphoranimine $(CF_3CH_2O)_3P{=}NSiMe_3$, and the mixture was stirred at room temperature for 2−4 h. The monomer $Cl_3P{=}NSiMe_3$ (1.12 g, 5 mmol, 20 equiv) was added to the solution, and the mixture was stirred at room temperature for 6 h; larger additions of $Cl_3P{=}NSiMe_3$ required up to 24 h in some cases. Termination of the living polymerization was achieved by addition of 119 mg of the phosphoranimine **2** (0.27 mmol, 1.1 equiv) to the reaction mixture, which was stirred overnight at room temperature. All volatiles were removed under reduced pressure, and the resultant residue was dissolved in 25 mL of dry THF. Subsequent treatment of this solution with 3 mL of a 2.0 M solution of sodium trifluoroethoxide, and purification by precipitation into deionized water (3×) and hexanes (2×), yielded the hydrolytically stable styryl-telechelic poly[bis(trifluoroethoxy)phosphazene] (typical yields ranged from 75% to 80%). Typical ^1H NMR ($CDCl_3$): $\delta = 7.37$ (d), 7.01 (d, 2H), 6.45 (m, 1H), 5.57 (d, 1H), 5.32 (d, 1H), 4.56 (br). ^{31}P NMR ($CDCl_3$): $\delta = -8.45$ (s).

General Synthesis of a Poly(methyl methacrylate)-*graft*-poly[bis(trifluoroethoxy)phosphazene] Copolymer (4−15). Prepolymer **3** (1.47 g, 1 equiv) was dissolved in 20 mL of dry THF. To this solution were added methyl methacrylate (0.96 g, 49 equiv) and AIBN (14.7 mg). The reaction mixture was heated to reflux and stirred for 48 h under a dry argon atmosphere. The reaction mixture was then concentrated and precipitated into hexanes three times to isolate the graft copolymer as an off-white solid (typical yields ranged from 80% to 85%). Polymers **4−15** all gave the same chemical shifts but differed in the ratios of signals. A general list of the ^1H and ^{31}P NMR shifts seen for all of the synthesized polymers is reported here. ^1H NMR ($CDCl_3$): $\delta = 7.37{-}7.45$ (br), 6.91−7.10 (br), 4.15−4.65 (br), 3.44−3.73 (br), 1.45−2.28 (br), 0.81−1.40 (br). ^{31}P NMR ($CDCl_3$): $\delta = -8.51$ (s).

Results and Discussion

Synthesis and Structural Characterization of Graft Copolymers. The living cationic polymerization of phosphoranimines is an effective method for the synthesis of mono- and ditelechelic polyphosphazenes.[14] Previous studies on the reactivity of these macromolecules have indicated that a terminal styrene moiety can be used to incorporate a polyphosphazene into a graft copolymer.[11] This method has now been adopted for the preparation of a series of poly(methyl methacrylate)-*graft*-poly[bis(trifluoroethoxy)phosphazene] copolymers. Tris(trifluoroethoxy)phosphoranimine was treated with 2 equiv of phosphorus pentachloride to generate the initiating species $[(CF_3CH_2O)_3P{=}N{-}PCl_3]^+[PCl_6]^-$. Reaction of this initiator with a given amount of $Cl_3P{=}NSiMe_3$ (**1**) gave living poly(dichlorophosphazene) chains with only one reactive chain end. Termination of these chains with phosphoranimine **2** yielded styryl-telechelic poly(dichlorophosphazene). Macromolecular displacement of the labile chlorine atoms with sodium trifluoroethoxide gave the hydrolytically stable, styryl-telechelic poly[bis(trifluoroethoxy)phosphazene] (**3**) (Scheme 1). These prepolymers were synthesized with 10, 20, 30, and 40 repeating units, with the chain lengths controlled by the ratio of PCl_5 to **1**. Copolymerization of **3** with methyl methacrylate, using azobis(isobutyronitrile) as a free radical initiator, gave poly(methyl methacrylate)-*graft*-poly[bis(trifluoroethoxy)phosphazene] copolymers (Scheme 2). The ratio of **3** to methyl methacrylate in the copolymerization affected

Table 1. Characterization Data for Graft Copolymers 4−15

polymer	graft length (repeating units)[a]	mol % of grafts[b]	M_w ($\times 10^3$ g/mol)	M_n ($\times 10^3$ g/mol)	PDI	T_g (°C)	T_{50}[c] (°C)	RI[d]
4	10	3.2	700	409	1.710	37	392	1.418
5		6.8	373	258	1.448	23	498	1.426
6		7.0	79.9	55.2	1.446	20	510	1.418
7	20	3.2	242	165	1.466	29	390	1.410
8		10.8	599	236	2.538	25	408	1.418
9		16.0	75.9	62.9	1.206	22	493	1.402
10	30	4.8	111	95.9	1.157	33	388	1.394
11		5.9	96.7	57.0	1.698	25	388	1.418
12		16.9	60.4	45.1	1.339	16	517	1.386
13	40	1.0	84.9	69.6	1.219	19	407	1.378
14		5.8	122	84.1	1.448	13	424	1.402
15		10.5	348	181	1.918	11	519	1.394

[a] Controlled through the monomer:initiator ratio used in the cationic polymerization of $Cl_3P{=}NSiMe_3$. [b] 1 mol % is defined as 1 grafted polyphosphazene chain per 100 repeating units of poly(methyl methacrylate) backbone; obtained from the ^{1}H NMR spectra by comparing integration for methyl ester protons at 3.6 ppm to OCH_2CF_3 protons at 4.5 ppm. [c] Taken as the temperature where 50% of the initial weight is lost. [d] Measured using the immersion method; under the conditions used, measurements are accurate to ±0.008.

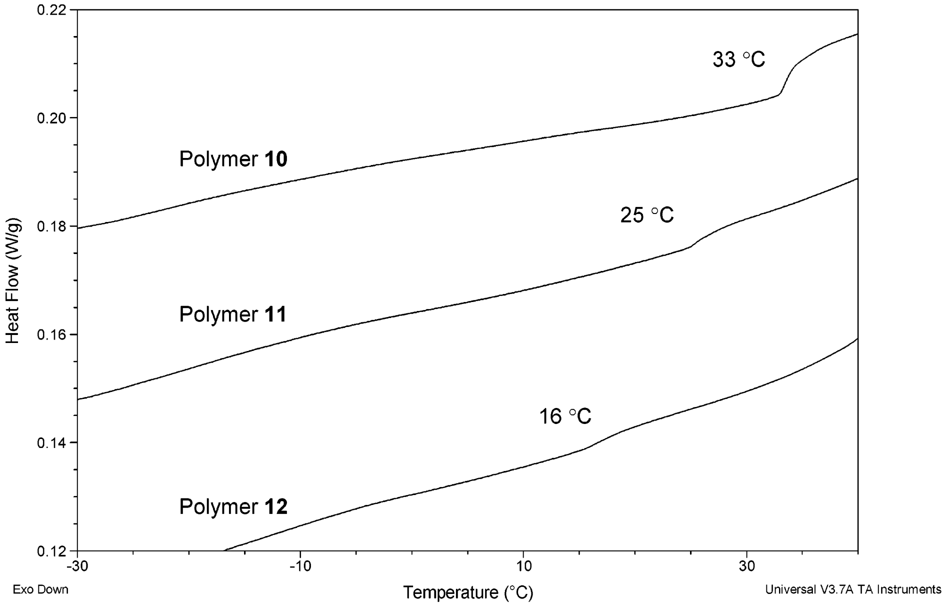


Figure 1. Glass transition temperatures for a series of graft copolymers with increasing frequency of 30 repeating unit poly[bis(trifluoroethoxy)phosphazene] grafts along the poly(methyl methacrylate) backbone.

the level of incorporation of the polyphosphazene grafts into the poly(methyl methacrylate) backbone. ^{1}H NMR spectroscopy indicated that the incorporation ranged from 1.0 to 16.9 mol % (i.e., 1 mol % is defined here as 1 grafted polyphosphazene chain per 100 repeat units of PMMA backbone). Gel permeation chromatography vs polystyrene standards revealed monomodal distributions for polymers **4**−**15**. The weight-average molecular weights ranged from 60.4 × 10^3 to 700 × 10^3 g/mol, and number-average molecular weights ranged from 45.1 × 10^3 to 409 × 10^3 g/mol (Table 1).

Thermal Transitions in the Graft Copolymers. Differential scanning calorimetry (DSC) was used to examine the thermal transitions of graft copolymers **4**−**15**. The most obvious effect of the incorporation of polyphosphazene grafts into poly(methyl methacrylate) was the lowered glass transition temperatures (T_g) compared to that of poly(methyl methacrylate) (PMMA) homopolymer. All the copolymers had a T_g below 40 °C (Table 1), while PMMA homopolymer has a reported T_g of 105 °C.[20] The T_g values of the copolymers were related to both the length and frequency of the polyphosphazene graft along the backbone. For a series of copolymers that contain grafts of the same length, the T_g of the copolymers decreased as the number of grafted chains along the backbone increased. Polymers **10**, **11**, and **12**, with 4.8%, 5.9%, and 16.9% of 30 repeating unit polyphosphazene grafts, respectively, illustrate this trend with respective T_g values of 33, 25, and 16 °C (Figure 1). The influence of the polyphosphazene grafts on the glass transition temperature is possibly due to a large increase in the free volume of the system. Poly[bis(trifluoroethoxy)phosphazene] homopolymer has a T_g at −66 °C, which indicates a high degree of chain mobility. The grafted polyphosphazene chains act like plasticizing agents by forcing the backbone PMMA chains apart and generating additional free volume in the polymer matrix. This allows enhanced overall macromolecular motion to occur at lower temperatures than would normally be the case.

The length of the grafted polyphosphazene chains also affects the glass transition temperature. For two copolymers with different graft lengths, but which have the same average frequency of grafts along the backbone, the copolymer with the longer grafts has the lower T_g. This is illustrated by polymers **4** and **7** (3.2% each of 10 and 20 repeating unit grafts, respectively), where the copolymer that contained the longer grafts

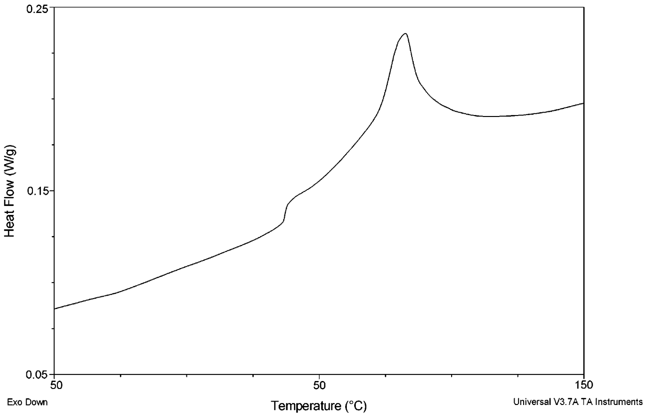


Figure 2. Typical differential scanning calorimetry data for a poly(methyl methacrylate)-*graft*-poly[bis(trifluoroethoxy)-phosphazene] copolymer, heated at 10 °C/min.

had the lower T_g (29 °C vs 37 °C) (Table 1). This effect is very similar to that found for other methacrylate polymers, where a lengthened alkyl ester chain on a methacrylate monomer causes a free volume increase in the corresponding polymer and a subsequent decrease in T_g.[21]

Increased crystallinity is another consequence of the incorporation of poly[bis(trifluoroethoxy)phosphazene] grafts into poly(methyl methacrylate). Although atactic PMMA homopolymer is considered to be completely amorphous, inclusion of the semicrystalline poly[bis-(trifluoroethoxy)phosphazene] grafts introduces microcrystalline regions into the graft copolymers.[22] Thus, T(1) transitions characteristic of microcrystalline domains in poly[bis(trifluoroethoxy)phosphazene] were detected by DSC measurements for most of the copolymers described here. (A representative DSC trace for a graft copolymer is given in Figure 2, showing a T(1) transition beginning at approximately 72 °C.[1]) It is possible that this is a consequence of polyphosphazene chains generating ordered regions between the PMMA chains rather than crystallization of the PMMA chains themselves. The T(1) values for the copolymers ranged from 40 to 72 °C, but no clear trend could be determined between the composition of the graft copolymer and its T(1) value or degree of crystallinity.

Thermal Stability of Graft Copolymers. Poly(methyl methacrylate) depolymerizes to monomer when heated above approximately 220 °C, as shown by the onset of the steepest portion of the curve in Figure 3. Thermogravimetric analysis (TGA) was used to study the thermal stability of the graft copolymers. For a series of copolymers that contained grafted chains of the same length, it was found that the T_{50} weight loss values increased steadily with the amount of incorporation of the poly[bis(trifluoroethoxy)phosphazene] grafts. This is attributed to the thermal stability of the polyphosphazene homopolymer being imparted into the graft copolymer or the grafts interrupting the mechanism of PMMA depolymerization. Poly[bis(trifluoroethoxy)phosphazene] homopolymer does not undergo a significant weight loss until approximately 380 °C, a process attributed to depolymerization to low molecular weight rings. Thus, small incorporations of this polymer into PMMA significantly increase the thermal stability of the system. Figure 3 shows the trend of increasing T_{50} values with increasing incorporation of polyphosphazene grafts for polymers **7**−**9**, with the onset of weight loss rising from approximately 200 to 375 °C. For the same series of copolymers, the residual *nonvolatile* yields decreased with increased loading of the grafts. This suggests that the mechanism for retardation of decomposition does not involve the formation of covalent cross-links, which would presumably increase the formation of nonvolatile residues.

Refractive Indices of Graft Copolymers. Poly(methyl methacrylate) is widely used in optical applications due to its clarity and refractive index (RI). The refractive indices of the graft copolymers were measured using the liquid immersion method. The incorporation of even a small amount of fluorine into a polymeric system can greatly reduce its RI.[23] The highly fluorinated poly[bis(trifluoroethoxy)phosphazene] units in graft copolymers **4**−**15** reduced the refractive index of PMMA homopolymer from 1.54 to approximately 1.41.[20] Although all the copolymers show reduced RI values when compared to that of PMMA homopolymer, only small differences in RI occur between the copolymers with the smallest and largest incorporation of polyphosphazene grafts (polymers **4** and **15**). This may be due

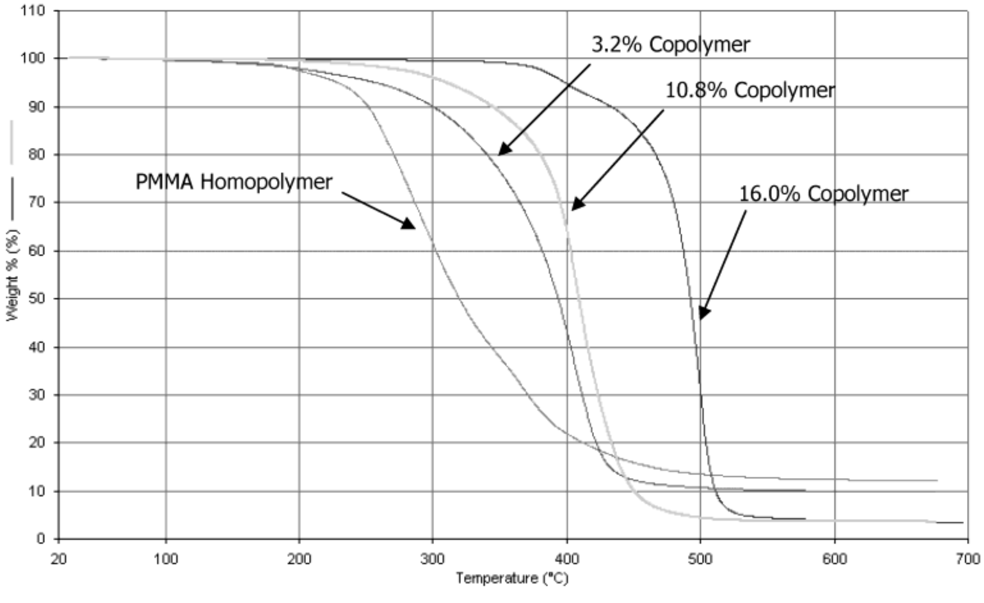


Figure 3. TGA data for poly(methyl methacrylate) homopolymer and a series of poly(methyl methacrylate)-*graft*-poly[bis-(trifluoroethoxy)phosphazene] copolymers that contain grafts of 20 repeating units; all samples were heated at 10 °C/min.

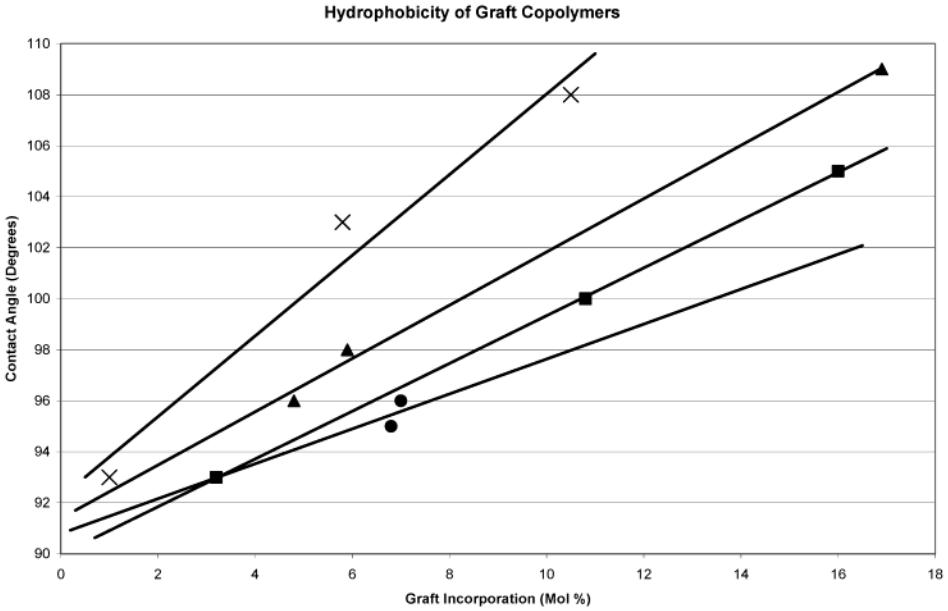


Figure 4. Contact angles of water droplets on films of graft copolymers with graft lengths of 10 (●), 20 (■), 30 (▲), and 40 (×) repeating units.

to the high weight percentages of fluorinated grafts found in all of the copolymers. Even polymer **4**, with only 3.2 mol % of 10 repeating unit grafts, has 44.5 wt % of polyphosphazene graft. This corresponds to almost 200 fluorine atoms for every 100 repeating units of PMMA backbone. It is possible that the graft copolymers contain such a large amount of fluorine that an asymptotic lower limit of refractive index has already been reached, and further increases in the fluorine content will not reduce the refractive index below 1.4. The incorporation of poly[bis(trifluoroethoxy)phosphazene] into the copolymers also affected the opacity of the materials. Films of the polyphosphazene graft copolymers were translucent whereas poly(methyl methacrylate) forms optically transparent films.

Hydrophobicity of Graft Copolymers. Poly[bis(trifluoroethoxy)phosphazene] is tough, fibrous material that is extremely hydrophobic due to its high fluorine content. Measurements of water droplets on films of poly[bis(trifluoroethoxy)phosphazene] show a contact angle of 109°. Water droplets on films of copolymers **4**−**15** gave angles between 93° and 109°, dependent on the amount of fluorine incorporated into the system. Figure 4 shows the increasing contact angles due to increasing incorporations of poly[bis(trifluoroethoxy)phosphazene] grafts into poly(methyl methacrylate). Higher loadings of the phosphazene component due to more grafts per poly(methyl methacrylate) chain steadily increase the contact angles of water on films of the copolymers. Contact angles are also increased by increases in the length of the grafted phosphazene chain, as demonstrated by polymers **8** and **15**. Each of these polymers contain between 10.5 and 11.0 mol % of grafted chains, but the grafts on polymer **15** are 40 repeating units in length compared to only 20 repeating units for polymer **8**. This gives a larger weight percentage of grafted phosphazene component and an increased contact angle (108° compared to 100°).

Conclusions

The living cationic polymerization of phosphoranimines was used to synthesize styryl-telechelic poly[bis(trifluoroethoxy)phosphazenes], which were copolymerized with methyl methacrylate to yield the first poly(methyl methacrylate)-*graft*-poly[bis(trifluoroethoxy)phosphazene] copolymers. The composition of the copolymers was confirmed using ^{1}H NMR and GPC, and this was then correlated to several thermal properties measured by DSC and TGA. The incorporation of poly[bis(trifluoroethoxy)phosphazene] lowers the glass transition temperatures and increases the crystallinity in the copolymers relative to PMMA homopolymer. An increase in measured T_{50} weight loss values was also detected as well as a decrease in nonvolatile residue yields. A clear relationship between the incorporation of poly[bis(trifluoroethoxy)phosphazene] and the hydrophobicity of the graft copolymer was detected through contact angle measurements. The refractive indices of the copolymers were also strongly influenced by the large amount of fluorine present in the grafts, although no structure−property trends could be identified.

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