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Improved Method for the Synthesis of Poly(organophosphazenes) and Hindered Cyclophosphazenes

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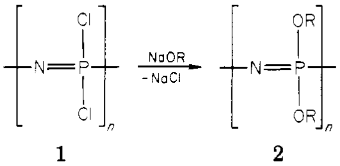
ABSTRACT: The use of tetra-n-butylammonium chloride or bromide as a solid/liquid phase-transfer agent and ion-pair separation catalyst has a dramatic accelerating effect on the reactions of poly(dichlorophosphazene) with sodium alkoxides or aryl oxides. This allows the synthesis of hitherto inaccessible high molecular weight polyphosphazenes or the preparation of known polymers under unusually mild experimental conditions. The same principles apply to the preparation of small-molecule cyclophosphazenes.

A large number of poly(alkoxyphosphazenes) and poly[(aryloxy)phosphazenes] (2) have been synthesized by the interaction of alkali metal alkoxides or aryl oxides with poly(dichlorophosphazene) (1) in organic media.[1-11]



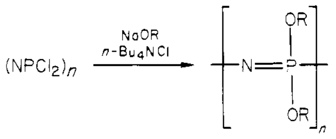
1 2

However, this method works well only when both the nucleophile and poly(dichlorophosphazene) are soluble in the same organic medium. If this requirement is not met, incomplete replacement of the halogen atoms may occur.

Many alkali metal alkoxides and aryl oxides are essentially insoluble in nonpolar organic media, and this restricts the number of different poly(organophosphazenes) that can be prepared. In addition, the attachment of bulky organic side groups such as aryloxy units to a phosphazene ring or chain requires the use of forcing reaction conditions that may cause partial depolymerization of the high polymer to cyclic oligomeric analogues.

We have now developed a modification to the conventional substitution process which overcomes both of the problems mentioned above. The method makes use of tetra-n-butylammonium chloride or bromide as a catalyst for use with sodium alkoxides or aryl oxides.[12] The tetraalkylammonium counterion serves to increase the lipophilicity and nucleophilicity of the oxyanions. Moreover, the interaction of a poorly soluble sodium alkoxide or aryl oxide with the tetraalkylammonium halide solubilizes the alkoxide as its alkylammonium salt. The result is a catalysis of the nucleophilic substitution process.

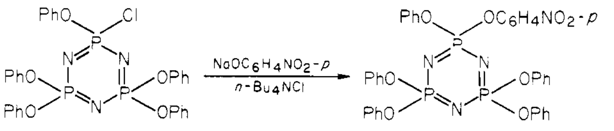
Scheme I



5, OR = OC_6H_5
6, OR = $OC_6H_4NO_2$-p
7, OR = OC_6H_4CHO-p
8, OR = $OC_6H_4COCH_3$-p
9, OR = OCH_2CF_3 and $OCH_2(CF_2)_5CF_2H$

Results

Model Reaction. The role of n-Bu$_4$NCl was monitored first for the model cyclic trimeric compound 3. In the absence of the alkylammonium halide, the interaction of 3 with sodium p-nitrophenoxide in dioxane resulted in no detectable formation of 4 after 1 week at 100 °C. The addition of n-Bu$_4$NCl to the reaction mixture was followed by a quantitative conversion of 3 to 4 within 30 min at the same temperature. The nonreactivity of 3 in the presence of sodium p-nitrophenoxide in dioxane is ascribed to both the insolubility of the nucleophile and its low nucleophilic character. Addition of the alkylammonium halide serves both to assist solubilization and to enhance its nucleophilicity through ion-pair separation.



3 4

High-Polymeric Reactions. Similarly, the presence of n-Bu$_4$NCl or n-Bu$_4$NBr has a powerful effect on the

0024-9297/83/2216-0719$01.50/0

reactions of sodium alkoxides or aryl oxides with poly(dichlorophosphazene) (**1**) in organic media. The rates of the substitution reactions are accelerated markedly, and lower reaction temperatures than normal can be used. As a result, high molecular weight poly[(aryloxy)phosphazenes] have been prepared under mild conditions, and a variety of hitherto inaccessible polymers with nitrophenoxy, aldehydic phenoxy, and acetylphenoxy side groups have been synthesized. Alkoxyphosphazene high polymers have also been prepared under unusually mild reaction conditions. These reactions are summarized in Scheme I.

The reaction of $(NPCl_2)_n$ with sodium phenoxide to yield **5** provides a good example of the technique. In the absence of the alkylammonium halide the reaction takes place slowly, often requiring 72 h at 120 °C before total replacement of chlorine can be achieved. The long reaction times at high temperatures usually result in depolymerization reactions, which yield **5** with a lower average molecular weight than would be expected from the chain length of its precursor, **1**. In the presence of n-Bu_4NCl, the reaction was complete after 8 h at 80 °C, and the product had a chain length comparable to that of the starting material, **1**.

Similar results were obtained with the other nucleophiles. Indeed, polymers **6**–**8** cannot be prepared in the absence of the catalyst. In addition, the preparation of (fluoroalkoxy)phosphazene polymers such as **9** and **10** is markedly facilitated by the presence of the alkylammonium halide. At 80 °C the reactions were complete in only 10–15 min. In the absence of the catalyst, the fluoroalkoxides are insoluble in toluene and the substitution reactions are slow and incomplete.

Because both (fluoroalkoxy)- and (aryloxy)phosphazene polymers are of technological and biomedical interest,[9-11] these catalyzed reactions may have an appreciable impact on the development of this field. In principle, the use of similar catalysts should also assist the rather difficult substitution reactions carried out with poly(difluorophosphazene), $(NPF_2)_n$, in fluorocarbon media.[13] This possibility is being examined.

Experimental Section

Reagents and Solvents. Hexachlorocyclotriphosphazene (mp 111–112 °C) was obtained from a trimer–tetramer mixture (Ethyl Corp.) after two fractional vacuum sublimations at 60 °C (0.1 torr), two recrystallizations from heptane and two further vacuum sublimations. Phenol, 4-hydroxybenzaldehyde, 4-nitrophenol, and 4-hydroxyacetophenone (Aldrich) were sublimed and stored in vacuo. Tetrabutylammonium bromide (Aldrich) was dried before use by azeotropic removal of the water from a benzene solution, followed by storage in vacuo. Tetrahydrofuran and dioxane (Fisher) were distilled from sodium–benzophenone. Toluene (Fisher) was distilled from CaH_2. Trifluoroethanol (Halocarbon) was dried over molecular sieves before use. Sodium hydride, as a 60% dispersion in oil (Aldrich), was used as received.

Analytical Techniques. Proton-decoupled ^{31}P NMR spectra were obtained in the FT mode at 40.5 MHz with a JEOL JNM-PS 100 spectrometer equipped with a Nicolet 1080 data processing system. Infrared spectra were obtained with a Perkin-Elmer 580 spectrometer. Polymer separations and molecular weight approximations were accomplished by gel permeation chromatography (Waters Associates ALC-201 instrument). A 4 ft × $^3/_8$ in. 10^6-Å Styragel column was used with a tetrahydrofuran solvent flow rate of 2.4 mL/min. Approximate calibration of the columns was accomplished by means of narrow molecular weight distribution polystyrene standards obtained from Waters Associates. Mass spectra were obtained with an AEI MS 902 mass spectrometer operated at an ionization potential of 20 eV. Elemental analyses were obtained on samples that were dried for at least 8 h in vacuo at 40–80 °C.

Synthesis of Poly(dichlorophosphazene) (1). Polymerization of $(NPCl_2)_3$ was carried out in degassed, sealed glass tubes, each containing about 200 g of purified $(NPCl_2)_3$. The sealed tubes were heated in a Freas Model 104 thermoregulated oven at 250 °C for 120 h. The tubes were agitated during polymerization such that a rocking motion was completed about once each minute. After completion of the polymerization, residual trimer was removed by vacuum sublimation at 55 °C (0.5 torr). To reduce differences in the poly(dichlorophosphazene) samples, only one polymerization tube was used for all the substitution reactions reported here in order to ensure that the comparisons were valid.

Synthesis of $N_3P_3Cl(OC_6H_5)_5$ (3). Phenol (13.5 g, 0.144 mol) was dissovled in tetrahydrofuran (75 mL) and this solution was added to sodium hydride (14 g, 0.35 mol) suspendend in tetrahydrofuran (75 mL). When the reaction was complete, additional tetrahydrofuran (200 mL) was added, and the reaction mixture was heated to 50 °C. The hot solution was filtered, and the warm filtrate was added dropwise to a cold (0 °C) solution of $(NPCl_2)_3$ (10 g, 0.028 mol) in tetrahydrofuran (100 mL). The reaction mixture was stirred for 12 h at 25 °C. The solvent was removed by means of a rotary evaporator. Toluene (50 mL) was added to the residue, the solution was filtered, and the product was purified by means of HPLC column chromatography. Recrystallization from heptane yielded 6.25 g (35%) of $N_3P_3Cl(OC_6H_5)_5$: mp 68 °C; mass spectrum, m/e 635 calcd, 635 found. A ^{31}P NMR spectrum of the product contained an AB_2 pattern ($\nu_a = 22.1$ ppm, $\nu_B = 6.90$ ppm, $J = 83.1$ Hz).

Synthesis of $N_3P_3(OC_6H_5)_5(OC_6H_4NO_2$-$p)$ (4). A mixture of sodium hydride (3.15 g, 0.078 mol), 4-nitrophenol (11.0 g, 0.78 mol), and chloropentaphenoxycyclotriphosphazene (25 g, 0.039 mol) in dioxane (100 mL) was stirred at reflux for 168 h.[14] The mixture was then cooled to room temperature. A ^{31}P NMR spectrum of the reaction mixture revealed an AB_2 spin system pattern identical with that of the starting material (**3**). This indicated that no reaction had occurred. The remaining reaction mixture was treated with n-Bu_4NBr (2 g, 0.006 mol) and stirred at reflux for 30 min, during which time the solution changed from bright orange to deep brown. The mixture was then cooled and filtered via Schlenk techniques, and the filtrate was concentrated to a volume of 40 mL and added slowly to hexane (300 mL) to yield a precipitate of **4** (18 g, 62%). The white solid was recrystallized twice from ethanol. A ^{31}P NMR spectrum of the product consisted of a singlet at 9.34 ppm (mp 128 °C). Mass spectrum, m/e 738 calcd, 738 found.

Synthesis of Poly(diphenoxyphosphazene) (5).[2] A solution of poly(dichlorophosphazene) (5 g, 0.04 mol) in dioxane (225 mL) was added during a 1-h period to a stirred solution of sodium phenoxide, prepared from sodium hydride (6.9 g, 0.17 mol) plus phenol (17 g, 0.172 mol), and tetra-n-butylammonium bromide (0.5 g, 0.0015 mol) in dioxane (300 mL). The reaction mixture was heated for 8 h at 80 °C and then cooled to room temperature. The polymer solution was concentrated to 80 mL under reduced pressure, and the solution was added to water (600 mL) in order to precipitate the polymer. The precipitate was collected, dissolved in THF (80 mL), filtered under pressure, and precipitated into water (600 mL) to remove sodium salts. The polymer was then thoroughly extracted by Soxhlet techniques for 96 h using pentane. It was soluble in THF, dioxane, and benzene. A ^{31}P NMR spectrum consisted of a sharp singlet at −19.33 ppm, which was indicative of total halogen replacement. Yield: 8 g (86%). Characterization data are listed in Table I.

Synthesis of Poly[bis(4-nitrophenoxy)phosphazene] (6). A solution of poly(dichlorophosphazene) (5 g, 0.04 mol) in dioxane (225 mL) was added over 1 h to a stirred solution of sodium p-nitrophenoxide,[14] prepared from sodium hydride (6.9 g, 0.17 mol) plus 4-nitrophenol (28 g, 0.20 mol) in dioxane (300 mL), and n-Bu_4NBr (0.5 g, 0.0015 mol). The reaction mixture was heated for 8 h at 75 °C and then cooled to room temperature. The solid components were filtered off and washed with large amounts of water to remove occluded sodium chloride and excess sodium 4-nitrophenol. The polymer was thoroughly Soxhlet extracted for 96 h with acetone and for 96 h with hexane. It was soluble in a hot THF/DMF mixture but insoluble in diethyl ether, dioxane, benzene, ethanol, and aromatic and aliphatic hydrocarbons. The ^{31}P NMR spectrum consisted of a sharp singlet at −14.36 ppm, indicative of total halogen replacement. Yield: 5.2 g (40%).

Synthesis of Poly[bis(4-formylphenoxy)phosphazene] (7). A solution of poly(dichlorophosphazene) (5 g, 0.04 mol) in dioxane

Table I
Characterization Data for High Polymers

compd		microanalysis[a, b]				GPC MW[c]	^{31}P NMR,[d] ppm	% yield[e]
		% C	% H	% N	% P			
5	calcd	62.33	4.32	6.06	13.41	>1 × 10^6	−19.33	86
	found	62.39	4.22	6.06	13.46			
6	calcd	44.86	2.50	13.08	9.65	>1 × 10^6	−14.36	40
	found	44.79	2.42	13.09	9.70			
7	calcd	58.53	3.48	4.87	10.80	>1 × 10^6	−19.40	50
	found	58.78	3.72	5.00	10.86			
8	calcd	60.95	4.44	4.44	9.84	>1 × 10^6	−19.18	40
	found	61.00	4.60	4.26	9.84			
9	calcd	19.75	1.64	5.76	12.75	>1 × 10^6	−7.20	51
	found	19.51	1.63	5.57	12.49			
10[f]	calcd	20.70	1.25	3.90		>1 × 10^6	−7.36	50
	found	19.64	1.63	5.71				

[a] Analytical data were obtained by Galbraith Laboratories. [b] Residual chlorine (<1%) was attributed to HCl bound as a salt rather than to unreacted P–Cl units. Evidence for this view was obtained from a correlation of the microanalyses and the reduction of the chlorine content following treatment with tertiary amines. [c] The values shown represent gel permeation chromatography results from different synthesis reactions. The peaks corresponded to GPC average values of at least 1 × 10^6. They appeared at the upper molecular weight limits of the instrument. The values shown were obtained by comparison with polystyrene standards. [d] All samples were proton decoupled and were interpreted as singlets. Chemical shift positions were relative to aqueous 85% H_3PO_4. A D_2O capillary lock was used. [e] These values represent yields obtained following repeated reprecipitations of the polymers, which is necessary for obtaining accurate elemental analysis. Crude yields were always higher than 90%. [f] An analysis showed 0.2% chlorine.

(225 mL) was added over a 1-h period to a stirred solution of the sodium salt of 4-hydroxybenzaldehyde, prepared from sodium hydride (6.9 g, 0.17 mol) plus 4-hydroxybenzaldehyde (25 g, 0.17 mol),[14] and tetrabutylammonium bromide (1.0 g, 0.0030 mol) in dioxane (300 mL). The reaction mixture was heated for 8 h at 80 °C and then cooled to room temperature. The polymer precipitated from solution on cooling. The solid components were filtered off and were washed with large amounts of water to remove occluded sodium salts. The polymer was thoroughly Soxhlet extracted for 96 h with ethanol and for 96 h with hexane. The polymer was soluble in dimethyl sulfoxide. A ^{31}P NMR spectrum consisted of a sharp singlet at −19.4 ppm, which was indicative of total halogen replacement. Yield: 5.8 g (50%).

Poly[bis(4-(methylcarbonyl)phenoxy)phosphazene] (8). A solution of poly(dichlorophosphazene) (5 g, 0.04 mol) in dioxane (225 mL) was added over a 1-h period to a stirred suspension of sodium 4-(methylcarbonyl)phenoxide, prepared from sodium hydride (6.9 g, 0.17 mol) plus 4-hydroxyacetophenone (26 g, 0.19 mol),[14] and tetrabutylammonium bromide (1.0 g, 0.0030 mol) in dioxane (300 mL). The reaction mixture was heated for 8 h at 80 °C and then cooled to room temperature. The polymer precipitated from solution on cooling. The solid components were filtered off and washed with large amounts of water to remove occluded sodium chloride and excess sodium 4-(methylcarbonyl)phenoxide. The polymer was thoroughly Soxhlet extracted for 96 h with acetone and for 96 h with hexane. It was soluble in hot dimethyl sulfoxide but was insoluble in diethyl ether, benzene, ethanol, and aliphatic hydrocarbons. The ^{31}P NMR spectrum consisted of a sharp singlet at −19.18 ppm, which was indicative of total halogen replacement. Yield: 5 g (40%). Characterization data are listed in Table I.

Synthesis of Poly[bis(trifluoroethoxy)phosphazene] (9).[1] A solution of poly(dichlorophosphazene) (5 g, 0.04 mol) in toluene (150 mL) was added over a 0.5-h period to a stirred suspension of sodium trifluoroethoxide, prepared from sodium hydride (17.24 g, 0.43 mol) plus trifluoroethanol (45 g, 0.45 mol), and tetrabutylammonium bromide (1.0 g, 0.003 mol) in hot toluene (300 mL). The reaction mixture was heated for 10 min at 80 °C and then cooled to room temperature. The polymer precipitated from solution. The solid components were filtered off and washed with large amounts of water to remove occluded sodium salts. The polymer was reprecipitated twice from acetone into water. It was then Soxhlet extracted for 96 h with hexane. The polymer was soluble in acetone, THF, and dioxane. The ^{31}P NMR spectrum consisted of a sharp singlet at −7.2 ppm, which was indicative of total halogen replacement. The polymer was a white, film-forming material. Yield: 5 g (51%).

Synthesis of Poly[(trifluoroethoxy)((dodecafluoroheptyl)oxy)phosphazene] (10). A solution of poly(dichlorophosphazene) (5 g, 0.04 mol) in toluene (150 mL) was added over a 0.5-h period to a stirred emulsion of the sodium salts of trifluoroethanol and dodecafluoroheptanol, prepared from sodium hydride (8 g, 0.2 mol), trifluoroethanol (10 g, 0.1 mol), and dodecafluoroheptanol (33.2 g, 0.1 mol), together with tetrabutylammonium bromide (1.0 g, 0.003 mol) in hot toluene (300 mL). The reaction mixture was heated for 15 min at 80 °C and then cooled to room temperature. The polymer precipitated from solution. The solid components were filtered off and washed with large amounts of water to ensure removal of occluded sodium salts. The polymer was reprecipitated twice from acetone into water and thoroughly Soxhlet extracted for 96 h with hexane. It was soluble in acetone, THF, and dioxane. The ^{31}P NMR spectrum consisted of a sharp singlet at −7.36 ppm. The polymer was a white, film-forming material. Yield: 50%.

Characterization of the High Polymers. All the polymers were soluble in organic media and were, therefore, un-cross-linked. As shown in Table I, the microanalyses corresponded to structures **5**–**10**. Less than 0.1% residual chlorine was detected in the polymers, an indication of the high efficiency of substitution. The ^{31}P NMR singlet spectra of the polymers provided confirmatory evidence for complete halogen replacement.

The infrared spectra of the polymers were consistent with the expected structures. All the polymers showed a characteristic P=N "stretching" absorption between 1320 and 1100 cm^{-1}. The characteristic nitro band for polymer **6** was detected at 1560 cm^{-1}. The characteristic carbonyl bands at 1705 and 1708 cm^{-1} were detected for polymers **7** and **8**, respectively.

The GPC-average molecular weights were above 1 × 10^6, values that are higher than those normally found for poly[(aryloxy)phosphazenes].

Acknowledgment. We thank the U.S. Army Reseach Office for support of this work.

Registry No. 3, 5032-39-3; 4, 85251-38-3; sodium phenoxide, 139-02-6; sodium 4-nitrophenoxide, 824-78-2; tetrabutylammonium bromide, 1643-19-2; $(NPCl_2)_3$, 940-71-6.

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(14) The sodium salts of 4-nitrophenol, 4-hydroxybenzaldehyde, and 4-hydroxyacetophenone are insoluble in boiling dioxane. They become soluble in the presence of tetrabutylammonium bromide.

Esterification Reaction of Poly[(chloromethyl)styrene] with Salts of Carboxylic Acids Using Phase-Transfer Catalysts

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ABSTRACT: The esterification reactions of poly[(chloromethyl)styrene] (polymer 1) with salts of carboxylic acids in solid–liquid or liquid–liquid two-phase systems were studied under mild conditions at room temperature using phase-transfer catalysts. In these reactions, the catalytic effects of a wide variety of crown ethers, quaternary ammonium salts, and a quaternary phosphonium salt were investigated. Tetrabutylammonium bromide (TBAB), tetrapentylammonium bromide (TPEAB), and tetrabutylphosphonium bromide (TBPB) showed excellent catalytic effects in the solid–liquid phase reaction between polymer 1 dissolved in an organic solvent and solid potassium acetate, and TBPB also showed an excellent catalytic effect in the liquid–liquid phase reaction between polymer 1 in an organic solvent and a saturated aqueous solution of potassium acetate. In contrast, crown ethers such as 18-crown-6 (CR6) and dicyclohexyl-18-crown-6 (DHCR) were better phase-transfer catalysts than the quaternary ammonium salts in the two-phase reaction of polymer 1 with potassium thioacetate.

Introduction

It is known that polymers with pendant chloromethyl groups are useful as polymeric supports[1] for the syntheses of polypeptides, polynucleotides, and polysaccharides and as starting polymers for the syntheses of other functional polymers[2] such as polymeric reagents, polymeric catalysts, polymeric carriers, polymeric photosensitizers, and photosensitive polymers[3]. Thus far, substitution reactions of the chloromethyl group in the polymer with a number of nucleophilic reagents have been widely carried out in aprotic polar solvents[4] such as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide, and hexamethylphosphoramide. Acceleration by some quaternary ammonium salts and crown ethers had been found[5] in the reactions of a chloromethyl group in the polymer with nucleophilic reagents in aprotic polar solvents; however, these reactions even proceed without the quaternary ammonium salt and crown ether in aprotic polar solvents. On the other hand, over the pase several years phase-transfer catalysis has been found to be useful[6] in many organic reactions. Recently, phase-transfer catalysis was also applied to syntheses of polymers such as polycarbonate[7], polyether[8], poly(thioether)[9], and polyester[10] and to modifications of polymers such as poly(vinyl chloride)[11], cross-linked poly[(chloromethyl)sytrene][12], and poly(1-chloro-2,3-epoxypropane)[13]. However, almost all of these reactions were carried out at elevated temperatures.

In earlier articles[14], we reported the successful reaction of poly[(chloromethyl)styrene] (polymer 1) with a number of nucleophilic reagents in a two-phase-transfer system consisting of an aprotic nonpolar solvent and a solid reagent using phase-transfer catalysts (PTCs) such as crown ethers and quaternary ammonium salts under mild reaction conditions. This simple, mild and economical method is very interesting for syntheses of functional polyers. Especially, esterification reactions of the chloromethyl group in the polymer with salts of carboxylic acids are important from the point of view of polymeric supports. In this article, we report in detail the substitution reactions of polymer 1 with salts of carboxylic acids in the two-phase system using PTCs under mild conditions.

Experimental Section

Materials. Solvents, Reagents, Catalysts, and Polymer. The solvents were purified in the usual way prior to use. Potassium acetate (KOAc) and potassium benzoate (KOBz) were recrystallized from methanol. Potassium thioacetate (KSAc) and potassium thiobenzoate (KSBz) were synthesized from the reactions of potassium hydroxide with the corresponding thioacids in methanol, and then they were recrystallized from methanol and 2-propanol. Reagent grade sodium acetate (NaOAc), sodium benzoate (NaOBz), 15-crown-5 (CR5), 18-crown-6 (CR6), dibenzo-18-crown-6 (DBCR), dicyclohexyl-18-crown-6 (DHCR), tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetrapropylammonium bromide (TPRAB), tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrabutylammonium hydrogen sulfate (TBAS), tetrabutylammonium perchlorate (TBAPC), tetrapentylammonium bromide (TPEAB), tetrahexylammonium bromide (THAB), tetraoctylammonium bromide (TOAB), benzyltrimethylammonium chloride (BTMAC), methyltrioctylammonium chloride (MTOAC), hexadecyltrimethylammonium chloride (HTMAC), tetrabutylphosphonium bromide (TBPB), and poly(ethylene oxide) (PEO) ($\bar{M}_w \cong 7500$) were used without further purification. Polymer 1 (the inherent viscosity of the polymer in benzene was 0.16 dL/g, measured at a concentration of 0.5 g/dL at 30 °C) was prepared in 90% yield by radical polymerization of chloromethylated styrene (mixture of 40% meta and 60% para) using AIBN in benzene at 60 °C for 8 h. The chlorine content (measured by elemental analysis) in

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