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# Macromolecular Backbone Rearrangements: A New Approach to the Synthesis of *N*-Phenyl-Substituted Polyurethanes

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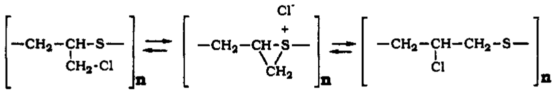
ABSTRACT: In analogy to the synthesis of polycarbonates, poly(Bisphenol A *N*-phenyliminocarbonate) (7) ($M_w$ = 85 000, by GPC relative to polystyrene standards), was synthesized from the disodium salt of Bisphenol A and phenyliminophosgene. 7 formed transparent, amorphous, mechanically strong films (tensile strength, 550 kg/cm$^2$; tensile modulus, 23 500 kg/cm$^2$; elongation at break, 2.8%). Upon heating to about 300–350 °C, 7 spontaneously rearranged to poly(Bisphenol A *N*-phenylurethane) (4). The rearrangement was a first-order reaction with an activation energy of 180 kJ/mol. The transformation of 7 to 4 was followed by FT-IR. Analysis of the polymer before and after heat treatment by gel permeation chromatography and low-angle laser light scattering indicated that the rearrangement proceeded without detectable backbone cleavage. The chemical structure of 4 was confirmed by $^1$H and $^{13}$C NMR. This polymer formed transparent, amorphous, and mechanically strong films (tensile strength, 567 kg/cm$^2$; tensile modulus, 23,800 kg/cm$^2$; elongation at break, 5.5%). Contrary to unsubstituted polyurethanes, 4 was thermally very stable. The onset of the decomposition exotherm was observed at 475 °C (DSC, in air, open pan), and the polymer started to lose weight at 504 °C (TGA, in air). Since N-substituted polyurethanes cannot be readily obtained by conventional polymerization reactions, the exceptionally clean, thermal rearrangement of 7 to 4 represents a rare case of a synthetically useful, polymeric backbone rearrangement.

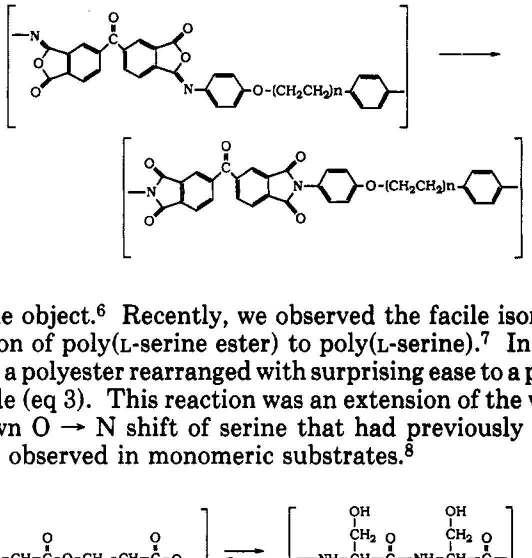
## Introduction

Macromolecules are usually prepared from monomeric starting materials by using a large number of different polymerization strategies.[1,2] A radically different synthetic approach is based on the use of macromolecular precursors for the synthesis of new polymers. This approach has been successfully employed in numerous instances where the target polymer could be obtained from the precursor polymer by the modification of functional groups located on pendent side chains. The synthesis of poly(vinyl alcohol) via hydrolysis of the side chain ester groups of poly(vinyl acetate) represents a well-known example for this type of polymer modification.[3] Contrary to the modification of polymer side chains, macromolecular transformations of the polymer backbone itself have only rarely been explored. Attempts to transform the backbone of high polymers tend to lead to structurally ill-defined products or to backbone cleavage due to degradative side reactions. Thus, the synthetically most useful backbone transformations have so far been limited to the preparation of carbon or silicon carbide fibers by controlled pyrolysis of various polymeric precursors.[4]

A literature survey revealed three instances in which polymer backbones have been quantitatively transformed by isomerization reactions. In a series of publications, Tirrell and Zussmen have reported on the surprisingly facile "backbone-assisted" isomerization of poly[(chloromethyl)thiirane] to poly(3-chlorothietane) (eq 1).[5] In addition, the isoimide–imide system (eq 2) is currently under investigation and may have significant synthetic utility: Since polyimides are extremely difficult to process, polyisoimides are prepared first, processed into shaped objects and only then the polyimide is formed by an isomerization reaction that does not disturb the preformed shape of the object.[6] Recently, we observed the facile isomerization of poly(L-serine ester) to poly(L-serine).[7] In this case, a polyester rearranged with surprising ease to a polyamide (eq 3). This reaction was an extension of the well-known O → N shift of serine that had previously only been observed in monomeric substrates.[8]



$$\left[-CH_2-\underset{CH_2\text{-}Cl}{\underset{|}{CH}}-S-\right]_n \rightleftarrows \left[-CH_2-\underset{CH_2}{CH}-\overset{\overset{Cl^-}{+}}{S}-\right]_n \rightleftarrows \left[-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-S-\right]_n \quad (1)$$



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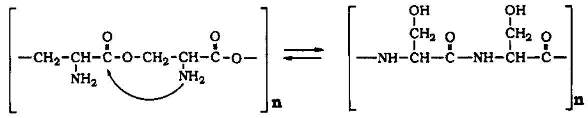

$$\left[-CH_2-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O-\right]_n \rightleftarrows \left[-NH-\overset{\overset{OH}{|}}{\overset{CH_2}{\overset{|}{CH}}}-\overset{O}{\overset{\|}{C}}-NH-\overset{\overset{OH}{|}}{\overset{CH_2}{\overset{|}{CH}}}-\overset{O}{\overset{\|}{C}}-\right]_n \quad (3)$$

In all three cases, a reaction that had originally been observed in monomeric species was successfully applied to macromolecules and had resulted in quantitative backbone rearrangements without significant degradation of the polymer chain. On the basis of these observations, we hypothesized that it should be possible to identify additional isomerization and rearrangement reactions that could be applied to the quantitative transformation of polymeric backbones. If the target polymer cannot be readily prepared while the precursor polymer is easily accessible, the identification of suitable backbone rearrangement reactions could be of considerable synthetic importance.

In this context, we identified the Chapman rearrangement of iminocarbonates to urethanes as a promising model system. This reaction (eq 4) had been studied for several monomeric iminocarbonates.[9] In particular, iminocarbonates carrying an electron-withdrawing substituent such as diethyl *N*-cyanoiminocarbonate (1) and the cyclic eth-

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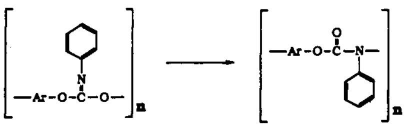
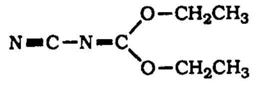
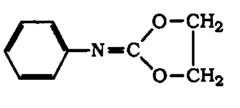
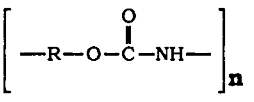

(4)

ylene *N*-phenyliminocarbonate (2) were found to rearrange quantitatively to the corresponding substituted urethanes at temperatures of about 100–200 °C. The question whether this rearrangement could be applied to the synthesis of polyurethanes had never been investigated.


**(1)**


**(2)**

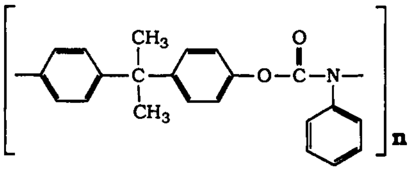
Polyurethanes are among the most widely studied and extensively used polymers.[10] Unsubstituted polyurethanes (3) carry a moderately reactive –NH– group in their backbone that severely limits their thermal stability.[11] The



$$\left[-R-O-\overset{O}{\overset{\|}{C}}-NH-\right]_n$$

**(3)**

thermal stability of polyurethanes can be increased by the replacement of the NH proton by an alkyl substituent.[11] An even higher degree of thermal stability may be achieved by the incorporation of an aromatic substituent. In particular, fully aromatic polyurethanes, such as for instance poly(Bisphenol A *N*-phenylurethane) (4), could be mechanically strong materials that would be stable at very high temperatures. Although some fully aromatic polyurethanes are known,[12] their material properties have not been characterized in detail, and in particular, poly(Bisphenol A *N*-phenylurethane) has not yet been prepared.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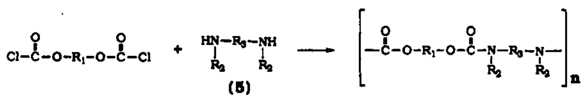
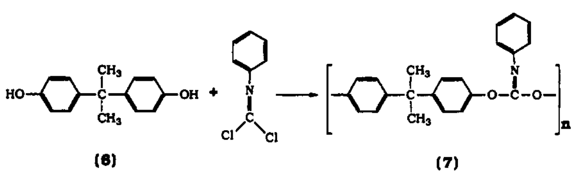
Currently, only two basic reactions are known for the synthesis of N-substituted polyurethanes: The ring-opening polymerization of N-substituted ethylene iminocarbonate (2) resulted in the formation of N-substituted polyurethanes.[9c,13] This reaction scheme was limited to the preparation of substituted derivatives of poly(ethylene urethane). A more general approach is based on the condensation polymerization of dichloroformates with substituted diamines (eq 5). Although a variety of N-alkyl substituted polyurethanes have been prepared in this way,[11] *N*-phenyl-substituted polyurethanes are not as readily accessible because of the high cost and limited availability of the required *N*-phenyl-substituted diamines (5). Thus, an alternative method for the synthesis of fully aromatic polyurethanes such as 4 would be of considerable practical utility.


(5)

We expected that *N*-phenyl-substituted poly(iminocarbonates) could be readily prepared from commercially available *N*-phenyliminophosgene and any suitable diphenols (eq 6). In analogy to the known behavior of monomeric iminocarbonates, the subsequent rearrangements of *N*-phenyl-substituted poly(iminocarbonates) could lead to fully aromatic polyurethanes. For our studies, we selected the widely used Bisphenol A (BPA) (6) as a model monomer and report here on the facile backbone rearrangement of poly(Bisphenol A *N*-phenyliminocarbonate) (7) to poly(Bisphenol A *N*-phenylurethane) (4).


(6)

## Experimental Section

**Materials.** Phenyl isocyanide dichloride (phenyliminophosgene, PIP), sodium, tetrabutylammonium bromide, and anhydrous *N*-methylpyrrolidinone (NMP) were purchased from Aldrich Chemical Co. Bisphenol A (BPA) was a gift from Shell Chemical Co. All solvents were HPLC grade.

**Measurements.** $^1H$ NMR and $^{13}C$ NMR spectra were obtained on a Varian XL 200-MHz spectrometer, using $CDCl_3$ as solvent. $^{13}C$ NMR were recorded at 50 MHz at 25 °C. Chloroform-*d* served both as solvent (30 mg of polymer/0.7 mL) and as the internal chemical shift reference. FT-IR spectra were recorded on a Matson Lygnus 100 spectrometer. GPC data were obtained with a HPLC/GPC system consisting of a Perkin-Elmer Model 410 pump, a Waters Model 410 RI detector, and a Perkin-Elmer model 3600 computerized data station. Two PL-gel GPC columns (300 mm × 7.7 mm, particle size 5 $\mu$m, pore size $10^3$ and $10^5$ Å, respectively) were placed in series and were operated at a flow rate of 1.0 mL/min in DMF (containing 0.1% LiBr) at room temperature. Weight-average molecular weights were calculated relative to polystyrene standards. The absolute weight average molecular weight ($M_w$) was determined by low-angle laser light scattering (LALLS) on a Chromatix KMX-6 at 25 °C in DMF. Intrinsic viscosity ($\eta$) was measured with an Ubbelohde type viscometer at 30 °C in chloroform.

**Mechanical Properties.** Thin films were prepared by solvent casting from a 10% (w/v) solution in methylene chloride at room temperature. After the films were allowed to dry in a slow stream of nitrogen overnight, the films were further dried in vacuum to constant weight (20 days). Samples of about 0.15-mm thickness, 40-mm length, and about 5–6-mm width were cut from the films and used for mechanical testing. Tensile strength, tensile modulus, elongation at yield, and break were determined on an Instron tensile tester Model 1122 at room temperature according to ASTM D882-83. Tensile values were calculated from the average of at least four measurements obtained from four separate specimens per polymer sample.

**Thermal Properties.** A Du Pont 910 differential scanning calorimeter (DSC) calibrated with indium was used to evaluate the thermal properties of polymer samples. The heating rate was 10 °C/min. Kinetic parameters were calculated by using a kinetic software package (Borchardt & Daniels) distributed by Du Pont. The thermal stability was determined on a Du Pont 951 thermogravimetric analyzer (TGA) at a heating rate of 20 °C/min under an atmosphere of nitrogen or air.

**Hydrolytic Degradation Studies.** Rectangular strips (2.3 cm × 1.1 cm × 0.05 cm, weight approximately 150 mg) were cut from solvent cast films. For 7, the films were incubated at 37 °C in phosphate buffer (0.1 M, pH 7.4). For 4, the films were incubated at 80 °C in either 1 N HCl or 1 N NaOH. The degradation process was followed by recording the weight change of individual samples and by measuring the residual polymer molecular weight after various intervals of exposure to the buffer solution.

**Synthesis. Preparation of Bisphenol A Disodium Salt.** A solution of sodium ethoxide (~1 M) was prepared by the addition of 15.6 g of sodium into 680 mL of absolute ethanol. The concentration of sodium ethoxide was determined by titration with standard HCl using phenol red as indicator. The sodium ethoxide solution was neutralized by the addition of an exactly equimolar amount of BPA. Thereafter, the solution was evaporated to dryness. The solid residue was rapidly crushed to a white powder and dried at 60 °C under high vacuum to constant weight. Care must be taken to avoid oxidation of the Bisphenol A disodium salt by atmospheric oxygen. Yield 80 g (98%).

**Preparation of 7.** Under an atomosphere of nitrogen, 29.97 g of finely powdered Bisphenol A disodium salt (0.110 mol) and 85 mL of anhydrous NMP were added into a three-necked flask. The resulting suspension was warmed to 45 °C. PIP (19.35 g; 0.111 mol) was slowly added into the well-stirred suspension over a period of 40 min. Stirring was continued for an additional 3.5 h. The disodium salt slowly dissolved. The solution turned brown and became viscous. The reaction mixture was diluted with 120 mL of methylene chloride, and the reaction was terminated by dropping the mixture into 1 L of methanol. The crude polymer, contaminated by sodium chloride precipitated and was collected by filtration. Yield 28.2 g (78%). For purification, the polymer was dissolved in methylene chloride, NaCl particles were removed by centrifugation, and a trace of particulate matter was removed by filtering the solution through a celite column. The clear polymer solution was then reprecipitated into methanol. Recovery 23 g (81%). The resulting poly(Bisphenol A *N*-phenyliminocarbonate) had a weight-average molecular weight of 85 000 (GPC, relative to polystyrene standards). $^{13}$C NMR ($CDCl_3$): $\delta$ 150.59, 147.61, 147.42, 144.87, 128.59, 127.81, 123.55, 122.67, 120.02, 42.38, 30.91 ppm. $^1$H NMR ($CDCl_3$): $\delta$ 7.01–7.28 (m, ArH; 13 H), 1.62 (s, $CH_3$; 6 H). IR (film on NaCl): see Figure 2A. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 78.89; H, 5.55; N, 4.10.

**Rearrangement of 7 to 4.** 7 (3.0 g) was placed into a 25-mL ampule. After flushing with nitrogen, the ampule was sealed under vacuum and placed into an oven preequilibrated at 350 °C. After 15 min, the ampule was cooled to room temperature, and the resulting polymer was used without further purification. $^{13}$C NMR ($CDCl_3$): see Figure 3. IR (film on NaCl): see Figure 2D. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 76.92; H, 5.53; N, 4.00.

**Diphenyl *N*-Phenyliminocarbonate (8).** Under nitrogen, 1.02 g of sodium phenoxide trihydrate (6 mmol) was suspended in 3 mL of anhydrous NMP. PIP (0.435 g; 2.5 mmol) in 1 mL of NMP was then dropped into the stirred suspension over 10 min. Stirring was continued for 30 min. The product was precipitated by pouring the reaction mixture into 50 mL of water. The aqueous suspension was extracted four times with ether (total volume 250 mL). Evaporation of ethyl ether gave a white solid. Yield 0.62 g (95%). The crude product was decolorized with active charcoal and recrystallized from hot hexane. Recovery 0.22 g (35%), mp 138–140 °C. IR (film on NaCl): $\nu_{C=N}$ = 1699 cm$^{-1}$. Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.93; H, 5.26; N, 4.61.

**Rearrangement of 8 to Phenyl *N,N*-Diphenylurethane (9).** One gram of recrystallized 8 was placed into a 10-mL ampule. After flushing with nitrogen, the ampule was sealed under vacuum and placed into an oven preequilibrated at 360 °C. After 30 min of reaction, the ampule was cooled to room temperature and the product was collected. Yield 0.95 g (95%). The crude product was recrystallized from hexane. Recovery 0.39 g (41%), mp 106–107 °C. IR (KBr pellet): $\nu_{C=O}$ = 1730 cm$^{-1}$. Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.67; H, 5.27; N, 4.82.

## Results and Discussion

**Synthesis of 7.** In analogy to the synthesis of polycarbonates from diphenols and phosgene, we reacted Bisphenol A with *N*-phenyliminophosgene (eq 6). Although the reaction mixture turned brown, indicating that some reaction occurred, no polymeric products could be identified by GPC. Since *N*-phenyliminophosgene appeared to be less reactive than phosgene itself,[14] we replaced the weakly nucleophilic BPA by its more nucleophilic disodium salt. Because of the insolubility of the disodium salt in organic solvents, we employed a classical interfacial polymerization reaction: an aqueous solution of disodium Bisphenol A was reacted with a solution of *N*-phenyliminophosgene in methylene chloride. Again, no polymeric products could be isolated. Attempts to improve the outcome of the reaction by either varying the molar ratio of the monomers or by the addition of a phase-transfer catalyst (tetrabutylammonium bromide) were not successful.

In order to enhance the reactivity of *N*-phenyliminophosgene by solvent effects, we switched to an interfacial system containing an aprotic polar solvent. When a two-phase system consisting of a 19 N aqueous solution of sodium hydroxide and a 3:1 (v/v) mixture of DMSO and THF as the organic phase was employed, 7 with a $M_w$ of 50 000 (GPC, relative to polystyrene standards) was obtained within 10 min. Longer reaction times resulted in a decrease of the molecular weight, possibly due to hydrolytic degradation of the polymer in the strongly basic reaction medium.

In an attempt to avoid the possible hydrolysis of the polymer, we suspended the disodium salt of BPA in anhydrous NMP, followed by the slow addition of a slight excess of *N*-phenyliminophosgene. This reaction mixture represented a heterogeneous reaction system consisting of a solid and a liquid phase. In the course of the reaction, the disodium salt gradually dissolved. The solution became viscous and turned brown. 7 with a weight-average molecular weight of about 85 000 (GPC, relative to polystyrene standards) and an intrinsic viscosity of 0.26 dL/g was obtained. Molecular weight analysis by LALLS revealed an absolute weight-average molecular weight of 37 500.

These results confirmed that *N*-phenyliminophosgene is far less reactive toward nucleophilic substitutions than phosgene. Consequently, interfacial polymerization techniques failed to yield high polymers, and the best results were obtained by the use of a heterogeneous reaction system in NMP.

**Confirmation of the Chemical Structure of 7.** The chemical structure of 7 was investigated by IR and $^1$H NMR spectroscopy. The IR spectrum (film on NaCl) showed a strong peak at 1691 cm$^{-1}$. In analogy to the characteristic C=N absorption of unsubstituted poly(Bisphenol A iminocarbonate)[15] at about 1675 cm$^{-1}$, we assigned the absorption at 1691 cm$^{-1}$ to the C=NPh stretching mode of 7. Aromatic bending modes characteristic of both para substitution (833 cm$^{-1}$) and monosubstitution (758, 695 cm$^{-1}$) were also observed. Whereas the IR spectrum of poly(Bisphenol A iminocarbonate) had a strong and sharp band at 3335 cm$^{-1}$ due to the N–H stretching mode, 7 had no absorptions above 3000 cm$^{-1}$.

In the $^1$H NMR spectrum of 7, the aromatic protons had chemical shifts in the range 7.01–7.28 ppm. The $CH_3$ proton resonance of the methyl groups of BPA was at 1.62 ppm. These chemical shifts are very close to those observed in the $^1$H NMR spectrum of unsubstituted poly(Bisphenol A iminocarbonate)[15]. As expected, the N–H

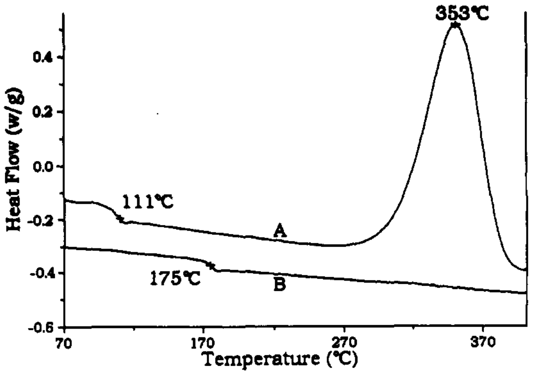


**Figure 1.** DSC thermograms for poly(Bisphenol A *N*-phenyliminocarbonate). Curve A: First run thermogram of virgin polymer. Curve B: Second run thermogram of same polymer sample. Both DSC thermograms were obtained at a heating rate of 10 °C/min.

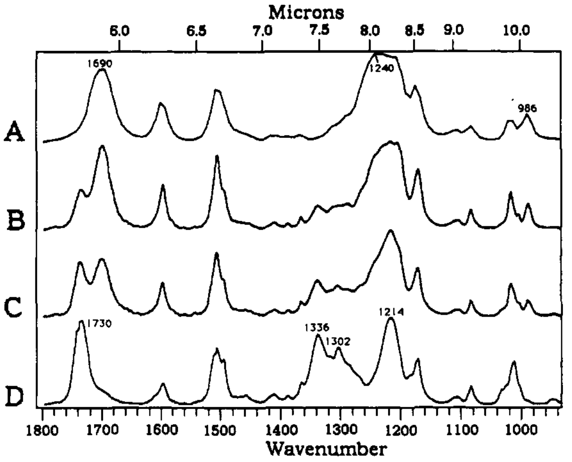


**Figure 2.** FT-IR spectra (films on NaCl) of poly(Bisphenol A *N*-phenyliminocarbonate) obtained after various periods of heat treatment at 305 °C. Curve A: Virgin polymer prior to heating. Curve B: After 15 min of heat treatment. Curve C: After 30 min of heat treatment. Curve D: After 120 min of heat treatment.

Table I
Molecular Weight Data

| polymer | $M_w$[a] | $M_w$[b] | $[\eta]$[c] | $n$[d] |
|---|---|---|---|---|
| 7[e] | 85 000 | 37 500 | 0.263 | 1.56 |
| 4[f] | 96 000 | 63 500 | 0.398 | 1.57 |

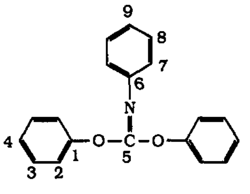
[a] Weight-average molecular weight determined by GPC relative to polystyrene standards. [b] Weight-average molecular weight determined by laser light scattering in DMF at 25 °C. [c] Intrinsic viscosity in dL/g, determined in chloroform at 25 °C. [d] Polydispersity calculated from GPC. [e] Polymer prior to thermal rearrangement. [f] Polymer after thermal rearrangement.

resonance at 5.79 ppm observed in unsubstituted poly(Bisphenol A iminocarbonate) was not seen in the spectrum of 7 (see Experimental Section for spectral data). $^{13}$C NMR showed 11 distinct carbon absorptions, corresponding to the 11 chemically nonequivalent carbon atoms present in the repeating unit of the polymer (see Experimental Section for spectral data).

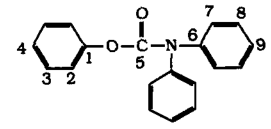
Overall, elemental analysis (see Experimental Section) and the spectral evidence obtained from IR and NMR spectroscopy confirmed that the polymer obtained from the reaction of *N*-phenyliminophosgene and BPA was indeed 7.

**Material Properties of 7.** Since 7 had not been prepared before, we investigated some of its material properties. 7 was easily soluble in most organic solvents, including methylene chloride, chloroform, tetrahydrofuran, *N*,*N*-dimethylformamide, toluene, and carbon tetrachloride. Solvent cast films of 7 were clear and transparent. X-ray crystallographic analysis showed no crystalline domains, indicating that the films were completely amorphous. This was confirmed by the lack of a melting endotherm in the DSC thermogram. Even at a relatively low molecular weight the films exhibited a high degree of mechanical strength (Table III). In this respect, 7 was very similar to unsubstituted poly(Bisphenol A iminocarbonate), which had previously been identified as a strong polymer with low ductility.[16,17] This observation is particularly noteworthy in view of the high ductility of the closely related poly(Bisphenol A carbonate).[18] The glass transition temperature ($T_g$) of 7 at 111 °C was in between the $T_g$ of unsubstituted poly(Bisphenol A iminocarbonate) (69 °C)[17] and poly(Bisphenol A carbonate) (159 °C).[18]

Table II
Chemical Shifts and Peak Assignments for the $^{13}$C NMR Spectra of Diphenyl *N*-Phenyliminocarbonate (8) and Phenyl *N*,*N*-Diphenylurethane (9)



(8)



(9)

| | carbon atom (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| compd | $C_1$ | $C_2$ | $C_3/C_8$ | $C_4/C_9$ | $C_5$ | $C_6$ | $C_7$ |
| 8 | 152.6 | 120.6 | 129.4/128.6 | 125.5/123.6 | 144.8 | 147.5 | 122.7 |
| 9 | 151.1 | 121.5 | 129.2/129.1 | 126.9/126.5 | 153.1 | 142.3 | 125.5 |

In view of the hydrophobic nature of 7, it is not surprising that the polymer absorbed only about 1% water during prolonged exposure to aqueous buffer solutions (37 °C, pH 7.4). This, however, did not prevent the rapid hydrolytic degradation of the polymer: Films of 7, incubated at 37 °C in phosphate buffer solution, became brittle within 55 days. GPC confirmed that the polymer had degraded to oligomeric species during this period.

**Thermal Rearrangement of 7.** The DSC thermogram of 7 showed a large exotherm with an onset at 305 °C (Figure 1). However, since TGA showed that 7 did not lose any weight up to 504 °C (in air), it was not clear whether the strong exotherm was caused by a thermal decomposition reaction.

In order to explore the thermal transformation of 7 in more detail, the polymer was heated in evacuated, sealed ampules to either 130, 200, or 305 °C. After predetermined heating times, the ampules were cooled and the heat-treated polymer samples were analyzed by GPC and FT-IR. At 130 °C, no changes in the molecular weight were observed. The polymer remained physically unchanged, and the FT-IR spectra before and after heat treatment were indistinguishable. At 200 °C, the molecular weight of the polymer increased, but no structural changes were detectable by FT-IR over a period of 120 min. At 305 °C, which is the onset temperature of the exotherm revealed by DSC, the molecular weight changed within 5 min and nearly doubled after 120 min of heating. The polydispersity of the polymer remained virtually constant during heat treatment. No low molecular weight degradation products were detectable. These observations excluded the occurrence of massive backbone degradation during heat treatment.

The molecular weight data obtained by GPC were relative to polystyrene standards and were not corrected for possible changes in the hydrodynamic volume of the polymer during heat treatment. It was therefore not clear

Table III
Physicomechanical Properties of Related Polymers of Bisphenol A[a]

| polymer[b] | tensile properties[c] |  | elongation[c] |  | thermal properties[d] |  | hydrolytic stability |
|---|---|---|---|---|---|---|---|
|  | strength, kg/cm$^2$ | modulus, kg/cm$^2$ | yield, % | break, % | $T_g$, °C | $T_d$, °C |  |
| polycarbonate (35 000)[e] | 625 | 22 000 | 5–7 | 100 | 149 | >350 | stable |
| poly(iminocarbonate) (100 000) | 500 | 21 500 | 3.5 | 4.0 | 69 | 135 | unstable |
| poly(*N*-phenyliminocarbonate) (85 000) | 550 | 23 500 | 2.8 | 2.8 | 111 | n/a | unstable |
| poly(*N*-phenylurethane) (96 000) | 567 | 23 800 | 3.4 | 5.5 | 175 | 470–90 | stable |

[a] Polymers were synthesized in our laboratory, except for poly(Bisphenol A carbonate), which was a commercial sample. [b] Numbers in parentheses refer to the weight-average molecular weight as determined by GPC relative to polystyrene standards. [c] According to ASTM standard D882-83. [d] Glass transition temperature ($T_g$) and decomposition temperature ($T_d$) were determined by DSC at 10 °C/min. $T_d$ represents the onset of the decomposition exotherm. [e] Data from ref 18.

whether the degree of polymerization indeed increased during heat treatment as indicated by the GPC data. In order to further investigate this point, the absolute weight-average molecular weight of the polymer prior to and after heat treatment was determined by LALLS. Our LALLS results (Table I) established unambiguously that the molecular weight of the polymer increased during heat treatment, probably due to the complete polymerization of residual, reactive end groups. Thus, the strong exotherm observed in the DSC thermogram of 7 had to be associated with a thermal rearrangement reaction and not with a thermal decomposition reaction.

In correspondence with this conclusion, a gradual structural change was observed in polymer samples exposed to 305 °C (Figure 2). The characteristic $\nu_{C=N}$ absorption of 7 at 1690 cm$^{-1}$ decreased while a new peak at 1730 cm$^{-1}$ emerged. This peak can conceivably be attributed to the aromatic carbonyl $\nu_{C=O}$ stretching mode. Peaks at 1240 and 986 cm$^{-1}$, which we assigned to the iminocarbonate bond, also decreased. New peaks at 1336 and 1302 cm$^{-1}$ were tentatively assigned to the $\nu_{C-O}$ and $\nu_{C-N}$ absorptions and provided supporting evidence for the formation of aromatic urethane bonds. The corresponding $\nu_{Ar-O}$ and/or $\nu_{Ar-N}$ stretching absorptions were observed around 1214 cm$^{-1}$. There results provide spectral evidence for the occurrence of a clean and well-defined thermal rearrangement reaction (eq 4) leading to the formation of 4.

By employing a kinetic software package (Borchardt & Daniels, distributed by Du Pont) the activation energy and reaction order of the rearrangement were calculated based on a single DSC scan from 30 to 450 °C with a linear heating rate of 10 °C/min. Based on this computer calculation, the rearrangement is a first-order reaction with an activation energy of 180.1 kJ/mol. These kinetic data are in agreement with the mechanism of the Chapman rearrangement, which is known to be an intramolecular reaction following first-order kinetics.[9a]

We found that the rate of the rearrangement reaction was somewhat influenced by the purity of the polymer sample: Carefully purified samples rearranged more slowly than samples containing (among other possible trace contaminants) about 0.1–1% sodium chloride. Since previous reports described the catalytic effect of metal salts on the rearrangement of monomeric iminocarbonates,[9] it is conceivable that small amounts of residual sodium chloride could have accelerated the rate of the rearrangement reaction.

In order to optimize the reaction conditions, samples of 7 containing about 0.1–1% sodium chloride were allowed to react in sealed ampules at temperatures ranging from 200 to 400 °C. We found that a clean, complete rearrangement can be achieved at 350 °C within 15 min. At lower reaction temperatures, it was difficult to obtain completely rearranged products, while at temperatures above 350 °C the polymer tended to partly decompose during heat treatment.

**Confirmation of the Chemical Structure of 4.** When using the optimized reaction conditions described above, no evidence for thermal decomposition was observed by FT-IR and GPC. The elemental analysis of the rearranged polymer was in agreement with the proposed structure of 4.

The nature of the rearrangement reaction and the structure of the obtained product were further investigated by $^{13}$C NMR spectroscopy. In an attempt to facilitate peak assignment and interpretation of the complex $^{13}$C NMR spectrum of the rearranged polymer, the thermal rearrangement of a monomeric model compound, 8, was studied. As ascertained by FT-IR, this model compound rearranged quantitatively to 9 within 35 min at 360 °C. The $^{13}$C NMR resonances of these two compounds and the corresponding peak assignments are summarized in Table II. These assignments were derived from the additivity of substituents on aromatic rings[19] and the peak intensities. No definitive assignments for $C_3/C_8$ and for $C_4/C_9$ were possible because of the small differences in chemical shifts between these pairs of carbon atoms. The conversion of the iminocarbonate group to a urethane group resulted in a downfield shift of 8 ppm of the carbonyl carbon resonance ($C_5$).

In the $^{13}$C NMR spectrum of 4, 15 distinct peaks were observed corresponding to the 15 chemically nonequivalent carbon atoms present in the repeating unit of the polymer (Figure 3). Although the $^{13}$C NMR spectrum of 4 was more complex than the spectrum of the monomeric model compound, it was possible to assign most of the polymer peaks based on the peak assignments made previously for 9. Only the aromatic methine carbons ($C_3$, $C_7$, $C_8$, $C_9$, $C_{13}$, $C_{14}$) in the range from 126.0 to 129.0 ppm (6 peaks) could not be assigned with confidence because of the small differences in chemical shift. The important carbonyl resonance for $C_5$ was found to be at the characteristic position for *N*-phenylurethane (153.2 ppm) and thus confirmed the presence of urethane backbone bonds.

The thermal rearrangement of 7 to 4 was expected to give rise to a random sequence of head–tail and tail–tail configurations in the rearranged polymer (Figure 4). The presence of these different configurations was confirmed by the observed splitting of the peaks assigned to $C_4$ and $C_{12}$.

**Material Properties of 4.** 4 dissolved readily in common organic solvents such as THF, DMF, and all common chlorinated hydrocarbons except carbon tetrachloride. It had a $T_g$ of 171 °C, which was about 60 °C higher than the $T_g$ of 7 (Table III). An important property of 4 is its high thermal stability: As determined by TGA, the polymer started to lose weight only at 504 °C in air and decomposed without charring. Under nitrogen, the

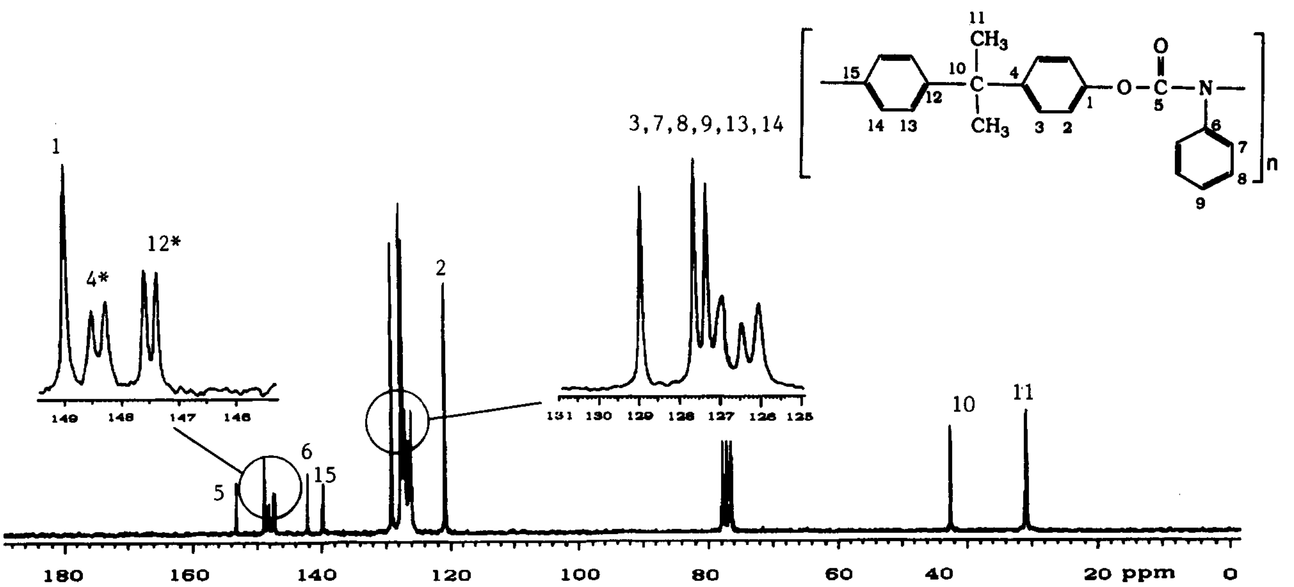


**Figure 3.** $^{13}$C NMR of the product obtained from poly(Bisphenol A *N*-phenyliminocarbonate) after heating to 350 °C for 15 min. The spectrum has 15 distinct peaks, corresponding to the 15 chemically distinct carbon atoms present in the repeating unit of poly(Bisphenol A *N*-phenylurethane). Inserts are magnified portions of the original spectrum as indicated. Doublets due to the presence of head–tail and tail–tail configurations are marked with a star (*).

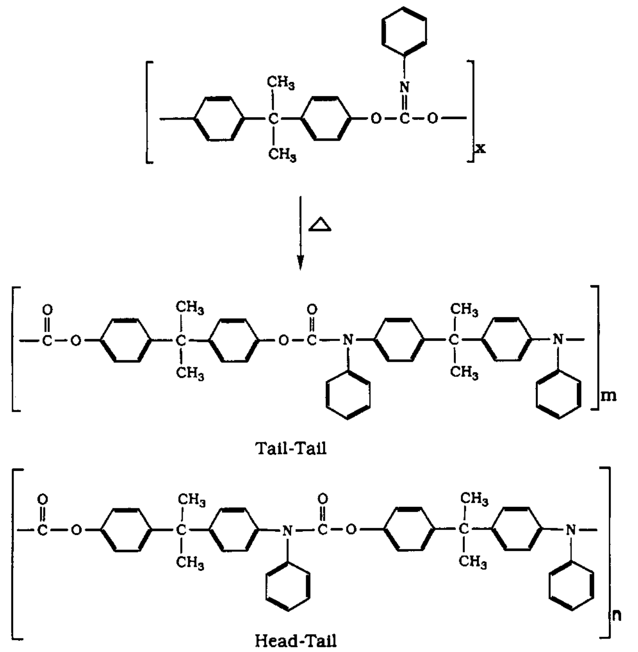


**Figure 4.** Backbone rearrangement process leading to head-tail and tail-tail type configurations. Poly(Bisphenol A *N*-phenylurethane), as obtained by the thermal rearrangement of poly(Bisphenol A *N*-phenyliminocarbonate), is therefore a random copolymer of repeating units linked together in either head–tail or tail–tail fashion.

onset of weight loss was at 538 °C and about 20% char remained at 600 °C (Figure 5). Using DSC, the onset of the polymer decomposition exotherm was observed at about 490 °C (air, open pan).

4 was a strong polymer whose mechanical strength was comparable to the strength of poly(Bisphenol A carbonate) and poly(Bisphenol A iminocarbonate) (Table III).

Finally we investigated the hydrolytic stability of 4. Whereas 7 degraded upon exposure to physiological buffer solution, 4 was highly resistant to hydrolytic degradation: Exposure of thin, solvent cast films of 4 to either 1 N NaOH or 1 N HCl at 80 °C for over 6 months resulted in no significant change in the molecular weight or the polydispersity of the polymer samples.

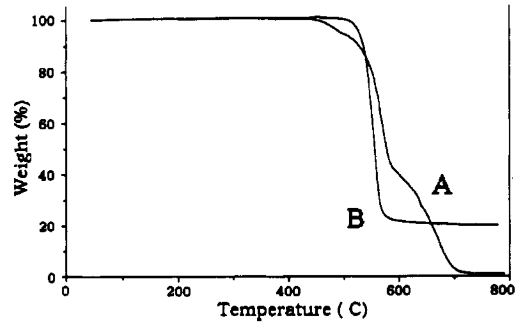


**Figure 5.** Thermogravimetric analysis (TGA) of poly(Bisphenol A *N*-phenylurethane). Curve A: Ambient air atmosphere. Curve B: Inert nitrogen atmosphere.

## Conclusions

Poly(Bisphenol A *N*-phenyliminocarbonate) was prepared for the first time from *N*-phenyliminophosgene and Bisphenol A. Since *N*-phenyliminophosgene is significantly less reactive than phosgene, the polymerization reaction has to be conducted under carefully optimized conditions. In our hands, the best results were obtained by the use of the sodium salt of Bisphenol A in a heterogeneous reaction system. In this study, 7 served as a readily available precursor for the synthesis of 4, a strong polymer with excellent thermal and hydrolytic stability. The thermal rearrangement of 7 to 4 was found to proceed quantitatively and without backbone cleavage within 15 min at 350 °C. The facile macromolecular backbone rearrangement of poly(iminocarbonates) to polyurethanes represents a new route to the synthesis of *N*-phenyl-substituted polyurethanes. In view of the fact that at least three macromolecular backbone rearrangements have been reported in the literature, it stands to reason that additional macromolecular rearrangement reactions will be identified in the future. In those instances in which a precursor polymer is cheaper and more readily available than the target polymer, macromolecular rearrangement reactions could become a valuable tool in polymer chemistry.

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**Registry No.** **6**(NMP) (copolymer), 132699-15-1; **6**(NMP) (SRU), 67422-08-6; **8**, 56500-07-3; **9**, 5416-45-5; NMP, 622-44-6; sodium phenoxide, 139-02-6.