Gaussian values of R_G/R_H, due to corrections for preaveraging. His bound appears to be consistent with the experimental deviation. On the basis of a more realistic description of hydrodynamic interactions, Fixman[6] provides a more conservative estimate of about an 8% change due to corrections for preaveraging, leaving a residual 7% discrepancy with experiment. Fixman's estimate is thus consistent with the Monte Carlo study of Guttman et al.[3] for this ratio, which they find to be $\langle S^2\rangle^{1/2}/R_H$(Kirkwood) = 1.40. Using this latter value in (7) and (8) with $\delta z_2^0 = 0$ leads to the estimate $z_3^0 \approx 0.003$. In addition, a value of z_3^0 can be estimated from the third virial coefficient at the Θ point. A_3 is readily calculated in lowest order to be

$$A_3 = [4\pi\langle S^2\rangle_0]^3 N_A^2 z_3^0/3M^3 \qquad (9)$$

Combining (9) with the data of Flory and Daoust[10,26] yields the rough estimate $z_3^0 \approx 0.006$ for polyisobutylene in benzene. This value is similar to the estimate $z_3^0 \approx 0.005$ of Oyama and Oono[10] for polystyrene in cyclohexane based on an assumed form of a semimicroscopic effective potential and estimates of microscopic parameters associated with this potential. Their self-consistent field study also gives an expression for $\langle S^2\rangle$ in general accord with (7).

The calculations in (6)–(8) can be utilized in a renormalization group analysis[9,12] to provide theoretical expressions that are valid for values of z_3^0 larger than those for which the simple perturbation results of (6)–(8) are meaningful. This renormalization procedure introduces corrections involving[8,9,16,24] logarithms of N. While z_3^0 must be system dependent, the above considerations indicate that it is very likely a rather small parameter. Given the above estimates of z_3^0 and the lack of observation of logarithmic corrections for lattice Monte Carlo chains, these logarithmic corrections are probably too small to be measured[12] and are hardly worth discussion, so the perturbation formulas (6)–(8) provide the first-order renormalization group predictions for the Θ region with the renormalized z_2, z_3 and N replacing the perturbative z_2^0, z_3^0, and N_0.

After submission of this communication, the work of Bruns[27] appeared, which extends the Monte Carlo calculations of Guttman et al. to longer chains. Bruns' long-chain extrapolation at the Θ point ($A_2 = 0$) gives the ratios $\langle S^2\rangle^{1/2}/R_H$(Kirkwood) = 1.464 ± 0.002 and $\langle R^2\rangle/6\langle S^2\rangle = 0.990$, *both of which* are in good agreement with (6)–(8) for $z_3^0 = 0.001$.

Our three-parameter calculations are in general accord with experiment and Monte Carlo simulations in the sense that our predictions, when used with Θ-chain data, lead to consistent order of magnitude estimates for z_3^0 and that our theory explains the shift from the Gaussian chain Θ point observed in the simulation data. We hope that our calculations stimulate further experimental and numerical simulations of Θ-point polymers to check our predictions.[3] The calculations also underscore the importance of considering expansion factors, the ratio of a quantity to its Θ-state value. Forming ratios like $\langle S^2\rangle/\langle S^2\rangle_\Theta$, $\langle R^2\rangle/\langle R^2\rangle_\Theta$, and $R_H/(R_H)_\Theta$ from (6)–(8) and then using the small estimated values of z_3^0 to expand it from denominators lead to the conclusion[28] that the expansion factors having z_3^0 enter in lowest order as $(z_3^0)^2$ and $z_3^0 z_2^0$. The expansion factors are, hence, less sensitive to the ternary interaction parameter than are the absolute magnitudes of the corresponding properties, a feature contributing to the good agreement of two-parameter renormalization group predictions with experiment.[29] In addition, expansion factors are found to be less sensitive to polydispersity corrections, making them perhaps the most suitable quantities for comparison between experiment and theory.

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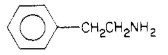
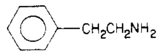
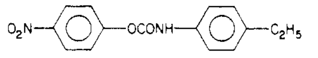
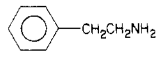
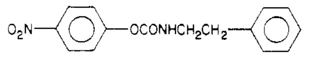
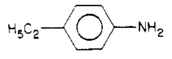
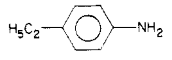
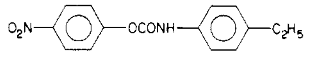
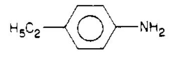
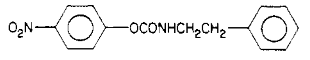
Structural Isomerism in Polycondensates. 3. Isomeric Polyureas from Aromatic Carbonates and Nonsymmetric Diamines

Structural isomerism in bipolycondensates from a symmetric (YccY) and a nonsymmetric (XabX) monomer is still a little investigated area. Korshak et al.[1,2] have prepared polyesters with a relatively small prevalence of –accb– enchainments (lowest value of *s*[3] achieved ca. 0.2) or –acca–/–bccb– enchainments (highest value of *s* achieved ca. 0.6) from terephthalic acid dichloride and nonsymmetric diols. Regular polyamides containing sequences of the type $(\text{accabccb})_{n/2}$, with $n > 100$ on the average ($s < 0.005$), as well as random polymers ($s \approx 0.5$), and a series of polymers with values of *s* between these two extremes have already been synthesized.[4]

The degree of regularity depends critically on the ratio of the reaction rates of the two functional groups in the nonsymmetric monomer (i.e., –aX and –bX) with the

Table I
Aminolysis Rate Constants of Carbonic Acid 4-Nitrophenyl Esters with Aliphatic and Aromatic Amines at 25 °C in Me_2SO

amine	ester	rate constant, L/(mol s)
	1	1.0×10^{3a}
		9.5×10^{2a}
		$3.6^{a,c}$
	1	1.0×10^{-2b}
		6.1×10^{-4b}
		1.0×10^{-5d}

[a] Measured by a stopped-flow technique with photometric detection at λ = 436 nm. [b] Measured in a UV spectrophotometer at λ = 350 nm. [c] Second substitution step of 1 with 2-phenethylamine. [d] Estimated value; slowest relevant reaction step.

Table II
Structural Regularity of Polyureas Obtained by Different Experimental Procedures

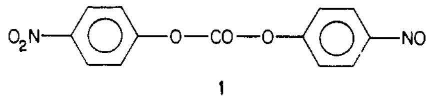
			s		
polymer	procedure	yield, %	^1H NMR[d]	^{13}C NMR[e]	theory
3	1 added slowly to 2[a]	95	0.05	0.06	<0.01
4	1 and 2 mixed rapidly[b]	93	0.89	0.90	0.99
5	2 added slowly to 1[c]	97	0.47	0.46	0.50

[a] 21.1 g (70 mmol) of 1 in 100 mL of Me_2SO was added during 6 h to 9.5 g (70 mmol) of 2 in 150 mL of Me_2SO at 25 °C. After 60 h of stirring at 25 °C, three-fourths of the solvent was evaporated and the polymers were precipitated with methanol. Polymers were washed with water and dried, redissolved in Me_2SO/LiCl (5%), reprecipitated with water/methanol, washed again with water, dried, stirred 2 days in methanol, and finally dried for several days at 60 °C (0.1 mmHg). [b] 1.02 g (7.5 mmol) of 2, 0.75 M in Me_2SO, and 2.28 g (7.5 mmol) of 1, 0.75 M in Me_2SO, were mixed in a continuous-flow apparatus[13] at 25 °C. Mixing times were <10 ms. Postmixing reaction and isolation were performed as described under a. [c] 0.89 g (6.5 mmol) of 2 in 10 mL of Me_2SO was slowly added to 1.99 g (6.5 mmol) of 1 in 10 mL Me_2SO at 25 °C. Postmixing reaction and isolation were performed as described under a. [d] 90 MHz (Bruker WH-90), in Me_2SO-d_6/LiCl (2%), at 120 °C. [e] 22.6 MHz (Bruker WH-90), in Me_2SO-d_6/LiCl (5%), at 30 and 50 °C.

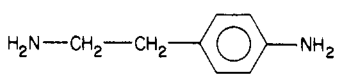
functional groups in the symmetric monomer (i.e., –cY), and as a consequence the rate constants of the reactions –aX + Yc– → –ac– and –bX + Yc– → –bc– as well as the relative concentrations of the functional groups are important in regulating structural isomerism. Preston et al.[5] recognized this first and used these concepts in the synthesis of polyamidehydrazides; it was also confirmed by others.[1,2,4,6-9]

We will show here for the first time how, from the same monomers, bipolycondensates can be obtained in one-step syntheses with either a large prevalence of –acca– and –bccb– enchainments or a large prevalence of –accb– sequences.

We have prepared polyureas from diamines and bis(4-nitrophenyl) carbonate (1) by solution polycondensation;[9] other authors have recently published similar results.[10] For the synthesis of structurally regular polyureas based on this scheme knowledge of the reaction rate constants in the system is required. Using the same approach as for polyamides,[4] we measured the reaction rate constants relevant in the aminolysis of bis(4-nitrophenyl) carbonate (1) with aliphatic and aromatic model amines. The results, summarized in Table I, show that the rate constants at 25 °C in Me_2SO are much higher for aliphatic than for aromatic amines; the rate constants for the former are larger than those for the latter by several orders of magnitudes. On the basis of these results 2-(4-aminophenyl)ethylamine (2) was chosen as nonsymmetric monomer for the polycondensation, assuming that the reaction rate constants from Table I are good approximations to the ones one would find with the diamine 2.



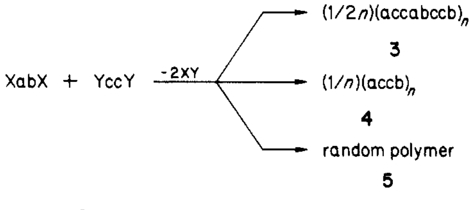
1
YccY



2
XabX

Further inspection of the values in Table I reveals that the reactivity of the urethanes from aliphatic or aromatic amines in aminolysis (i.e., the reaction in which the second 4-nitrophenyl group from the carbonate is eliminated) is different from the reactivity of the carbonate. Except for the reaction of an aliphatic amine with a urethane from an aromatic amine, the aminolysis of the urethanes is much slower than that of the carbonate. This is of paramount importance in the synthesis of polymers in which sequences of the type (accb) are prevailing.[11,12]

Using different reaction procedures we prepared the isomeric polymers 3, 4, and 5.



Values of s^3 of (i) <0.01, (ii) 0.99, and (iii) 0.50, respectively, are expected from theoretical considerations[12] if (i) the carbonate is slowly added to the diamine, (ii) both are mixed rapidly, and (iii) the diamine is slowly added to the carbonate, respectively. Experimentally it was possible to obtain the isomeric polymers 3 and 4 with s values of 0.05 and 0.90, besides a random polymer, 5, with s = 0.47, where the values for s were evaluated by ^1H and ^{13}C NMR (see Table II).

For polymer 3, in which –acca–/–bccb– sequences prevail, the experimentally found structural regularity agrees well with the theoretically expected value, and the same is true for polymer 5, which is structurally irregular. In

Table III
Results of Characterization of Polyureas

	polymer		
	3	4	5
s	0.05	0.89	0.47
$[\eta]$,[a] dL/g	0.38	0.33	0.57
$\bar{M}_n(^1H\ NMR)$[b]	3200	1700	4300
$\bar{M}_n$(VPO)[c]	2800	2000	
$\bar{M}_w$(SE)[d]			5000
$\bar{M}_z$(SE)[d]			11600
T_t,[e] °C	363	356	353
ΔH_t,[e] kJ/mol	78	62	54
solubility[f] (nonsolvent/solvent ratio)	0.38	0.50	0.54
WAXS band: 2θ,[g] deg	20.5	19.8 (sh)	20.0
	21.6 (sh)	21.1	21.3
	25.7	26.0	25.5

[a] In Me_2SO/LiCl (2%) at 30 °C. [b] By end group analysis. [c] The polymers were N-trifluoroacetylated by trifluoroacetic anhydride in methylene chloride under nitrogen,[15,16] and $\bar{M}_n$ was determined by VPO in acetone at 25 °C. Degrees of trifluoroacetylation, determined by quantitative ^{19}F NMR (Bruker WH-90), were 0.46 (3) and 0.47 (4). The intrinsic viscosity of 4 dropped to 0.11 dL/g on trifluoroacetylation but increased again to 0.27 dL/g on hydrolysis of the trifluoroacetylamide groups. [d] By sedimentation equilibrium runs in DMF/LiCl (0.03%) at 30 °C (Beckman E), with spectrophotometric determination of concentration at λ = 284 nm. [e] By DSC (Mettler 30). The first endothermal transition was measured at different heating rates, and transition temperatures were obtained by extrapolation to zero heating rate. Results are averages of at least three runs. [f] See ref 14. [g] From wide-angle X-ray diffraction (Seiffert). "sh" stands for "shoulder".

the case of the polymer with essentially head-to-tail structure, **4**, which is by far the most regular one of this structural type described to date, the observed regularity is still substantially lower than the theoretical value. Transamidation in the polymer chain does not seem likely under the chosen reaction conditions, and we attribute the discrepancy between experiment and theory to the fact that the very high reaction rates cause the polycondensation to be partially mass transport controlled, even though the rate of mixing was rather high. Molecular mass average of the polymers **3**, **4**, and **5** were obtained by dilute solution viscometry, vapor phase osmometry, and ultracentrifugation. Structural characterization was performed by ^1H and ^{13}C NMR, IR, differential scanning calorimetry, and WAXS. Solubility was determined as reported previously.[13,14] Results are collected in Table III.

Melting points (i.e., the first endothermal transition) of the three polymers are surprisingly similar, contrary to the experience with polyamides,[4,7] where structurally regular and irregular polymers melt at temperatures rather far apart. The enthalpies of this process are larger for the structurally regular polymers than for the irregular one, as one would expect. Solubility is somewhat lower in **3** than in the other two samples, but **4** is almost as soluble as **5**. Part of this surprising phenomenon might be due to the fact that the irregular polymer, **5**, is of higher molecular mass than the two relatively regular ones.

Structural regularity is indeed controllable in polyureas, and relatively high degrees of regularity can be achieved for head-to-tail as well as for head-to-head/tail-to-tail polymers.

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(11) In the extreme case where –bX reacts very much more slowly than –aX, and where –accY and –bccY react very much more slowly than YccY, the dimer XbaccY is formed almost exclusively in the early stages of the reaction. This then polymerizes to $(1/n)X(bacc)_nY$, and s = 1.

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Poly(ethylene imine)–Sodium Iodide Complexes

Polymers offer the potential of being used as solid electrolytes because of their ability to be formed into thin films and the ability of some polymers to dissolve salts and transport ions. Poly(ethylene oxide) (PEO) has been shown to interact so strongly with some of the alkali metal salts that a high-melting crystalline complex is formed which involves approximately 4 mol of monomer units per mole of salt.[1] Although early work focused on this crystal complex, it is now generally believed that the transport of ions occurs primarily in the noncrystalline regions of the polymer.[2-4] The crystal complex is a manifestation of the strong interaction between ions and polymer and serves the useful purpose of providing mechanical rigidity at temperatures between 60 and 180 °C where the polymer would otherwise flow. A few other polymers containing high concentration of polar groups and high flexible chains have been reported to dissolve salts. These include poly(propylene oxide)[5-7] ($-[CH(CH_3)CH_2O]_n-$), poly(epichlorohydrin)[8] ($-[CH[CH_2Cl)CH_2O]_n-$), and, more recently, poly(ethylene succinate)[9,10] ($-[O(CH_2)_2-OC(O)-(CH_2)_2C(O)]_n-$). We now present evidence to indicate that linear poly(ethylene imine) ($-[CH_2CH_2NH)]_n-$) can dissolve salts and, in the case of NaI, form a high-melting crystalline complex.

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