Polyurethane Networks Bearing Dendritic Wedges: Synthesis and Some Properties

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ABSTRACT: Polyurethane networks bearing dendritic wedges of the second, third and fourth generation were prepared by polymerization of dendritic diols of the corresponding generation with a commercially available triisocyanate (Desmodur RFE). The formation of a three-dimensional network was greatly influenced by the shielding effect especially of dendritic wedges of generation four. This phenomenon led to an increase of the sol fraction with rising generation number. The swelling behavior of polyurethane networks was studied by means of molecular dynamics simulations and the results were compared, in a qualitative sense, with experimental data. As opposed to the theoretical data for perfect networks, the experimental swelling ratio increased as a function of generation number. The discrepancy between molecular simulations and experimental data was attributed to the imperfect character, i.e., the presence of defects, of synthesized networks comprising dendritic wedges of higher generations. Since the cross-linker Desmodur RFE contains phosphorus, ^{31}P NMR was applied to reveal the effect of dendritic wedges on the mobility of junction points. Both the line widths and T_1 relaxation data proved to be sensitive to the effect of the generation number on the mobility of network junctions.

I. Introduction

In general, the properties of polymeric networks depend on a number of factors, including the length and flexibility of the chains between two-junction points.[1] To study the effect of the mobility of elastic chains and cross-link points in some detail, we prepared polymeric networks with a molecular structure as schematically shown in Figure 1. The polymeric networks contain dendritic wedges of different generations, chemically attached in the middle of each network chain. These dendritic wedges can be seen as nanofillers distributed homogeneously throughout the network. These fillers may restrict the mobility of elastic chains, depending on the generation number, i.e., size of the wedges.

The networks were prepared by polymerization of dendritic diols with a triisocyanate (Desmodur RFE) as shown in Figure 2. In analogy with our previous works,[2] we have used here Fréchet-type poly(ether) dendritic wedges[3] of generations 2, 3, and 4. Since each junction point contains a phosphorus atom, we have used ^{31}P-relaxation NMR to study the network mobility as a function of dendrimer generation. Furthermore, the effect of these dendritic wedges on the swelling behavior has been examined using molecular dynamics simulations and the results have been compared with experimental data.

II. Experimental Section

Materials and Synthesis. The triisocyanate Desmodur RFE was obtained from Bayer and recrystallized from dichloromethane to give white crystals with isocyanate functionality of three. All the dendritic wedges were synthesized according to the procedure described previously.[2a] Generally, the polymerization was carried out by dissolving a stoichiometric amount of dendritic wedges and triisocyanate ([−NCO]/[−OH] = 1) in dried tetrahydrofuran (THF) under a N_2 atmosphere. After adding a small amount of dibutyltin acetate (DBTA; Merck) and subsequent evaporation of THF under reduced pressure, the mixture was heated overnight at 60 °C in an oven under N_2. As revealed by FT-IR measurements, this procedure led generally to the complete disappearance of all isocyanate groups. Only for dendritic wedges of generation four, a small amount of unreacted isocyanate groups could be detected after polymerization. Throughout the text, the polyurethane networks are designated according to the code “PUN-G*X*”, where *X* is the generation number of the dendritic wedges.

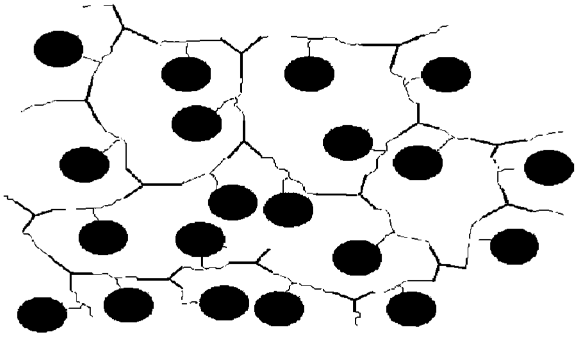

Figure 1. Schematic representation of a polymer network bearing large groups, which are chemically attached in the middle of each elastic chain.

Swelling Experiments. The degree of swelling was determined by swelling about 120 mg powder for 48 h in THF at 35 °C. The gel was filtered over a glass filter and the neat residue was weighed. Then the residue was dried at 70 °C under vacuum for 1 h. The dried residue was weighed again. The swelling procedure (2 days at 35 °C in THF) was repeated for the dried residue (gel fraction). Assuming that the difference in density between THF and the network is small, the swelling ratio is defined in the first approximation as the weight in the swollen state divided by the weight of the dried gel, i.e., without the sol fraction.

Differential Scanning Calorimetry (DSC). The DSC experiments were conducted on a Perkin-Elmer DSC-7 at a rate of 10 °C/min under a N_2 atmosphere. The glass transition temperatures were determined from the second heating runs.

Molecular Modeling Calculations. Models for the polyurethane networks containing second, third, and fourth generation dendritic wedges have been constructed by the means of the builder facility of the InsightII-based package of MSI,[4] which was running on a Silicon Graphics O^2 workstation. Force field calculations were performed using Discover version 97.0 on an SGI Power Challenge. Two different force fields were employed, viz., CVFF (Consistent Valence Force Field) and CVFFREP. CVFFREP is exactly the same as CVFF except

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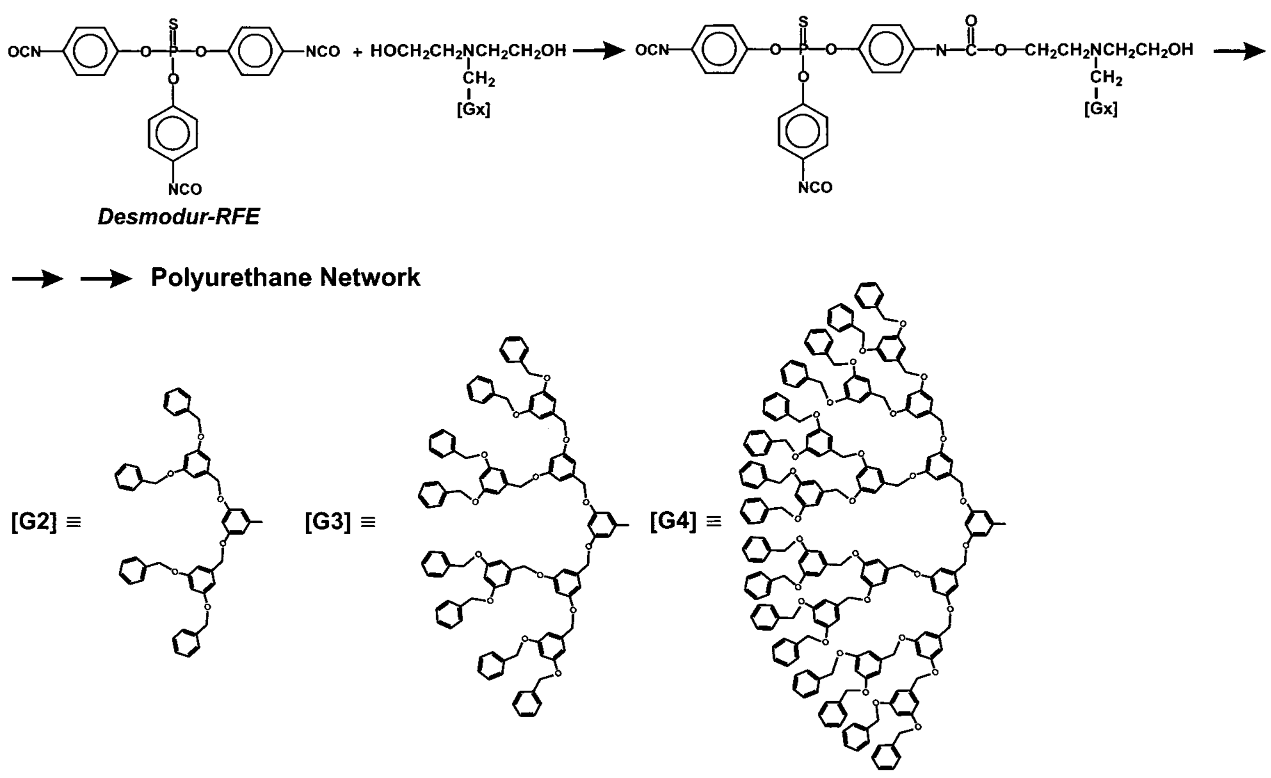

Figure 2. General synthetic scheme used in the present study.

with respect to the description of the nonbonded interactions. In CVFFREP the Columbic interactions are completely neglected, and as far as the van der Waals interactions are concerned, only the repulsive terms are taken into account. As such, when performing simulations using CVFFREP the molecule will expand as much as possible and the force field can therefore be considered as a model for a very good solvent. CVFF on the other hand may be considered as a model for a very poor solvent. This procedure has been applied previously to simulate classical dendrimers[5] and side chain dendritic polymers.[2a] All network models were first energy minimized until the maximum energy derivative was less than 1.0 kcal/mol·Å. Next, a simulated annealing run was performed. The starting temperature was 1500 K, the final temperature was 300 K, and the temperature step was 240 K. At each temperature, the simulation time was 5 ps. The final structures obtained at 300 K were consequently subjected to new simulations in order to generate 250 configurations of each of the network models at room temperature. Again, each structure was first energy minimized until the maximum energy derivative was less than 1.0 kcal/mol·Å. The structure was then equilibrated at 300 K for 10 ps after which every 250th configuration was stored until 250 configurations were obtained. Note that this time spacing does not guarantee completely uncorrelated configurations. In all MD runs, the time step was chosen to be 1 fs, the temperature was controlled by direct velocity scaling, and the equations of motion were integrated using the default Verlet velocity integrator. The summation method for evaluating the nonbonded interactions was set to no cutoff, i.e., all bonded interactions were taken into account, and a distance-dependent dielectric constant was employed. Average radii of gyration and average neighboring P−P distances taking all configurations into account were obtained using the Amorphous_Cell module.

Obviously, considering the size of the systems under study, ideal simulation conditions are hard to achieve. Ideally, one would like to study different starting configurations, have longer equilibration times etc. The longest simulation presented here already took 8 days of computing time on 4196 MHz R10000 processors. Only for the system containing G3 dendrimers, the 300 K simulation was carried out twice as long with no significant change of the main average property of interest (radii of gyration). In addition, for the system containing G4 dendrimers, two simulating annealing runs starting with different structures were carried out. Again, no significant change in the average radius of gyration was observed.

^{31}P NMR Experiments. Wide-line solid state ^{31}P NMR spectra and a T_1 relaxation time were determined on a Varian Inova 400 MHz spectrometer operating at a ^{31}P frequency of 161.9 MHz. A wide-line probe was used for the experiments. A single-pulse excitation was used to record the wide-line spectra. An inversion recovery method was used to obtain T_1 values. All experiments were performed with high-power proton decoupling. The 90° pulse widths were 5 and 4.8 μs for ^{1}H and ^{31}P, respectively. The spectral width was 2 MHz. The recycle time was 80 s. ^{31}P chemical shifts were referenced to 85 wt % water solution of H_3PO_4 by setting the peak position to 0 ppm. The experiments were performed on the gel fractions of samples and on partially swollen samples in THF. The samples were placed in a glass tube. Partially swollen samples were obtained by adding a certain amount of the solvent and storing samples at room temperature for 1 day before measurements. To prevent evaporation of the solvent, the tube was sealed. The measurements were performed at room temperature.

III. Results and Discussion

A. Synthesis, Differential Scanning Calorimetry, and Swelling Experiments. The synthetic scheme shown in Figure 2 should result in a network which is chemically heterogeneous; that is, it consists of a polyurethane main chain bearing polyether side groups. As a consequence, the possibility of phase separation during the cross-linking reaction should be taken into account. According to DSC measurements, the polyurethane networks of different generations display a single glass transition temperature (see Figure 3). This rules out the possibility of phase separation at least on a macroscopic scale. In contrast to dendritic wedges, the glass transition temperature of polyurethane networks decreases with increasing generation number (Table 1). This might be due to a larger sol fraction at higher

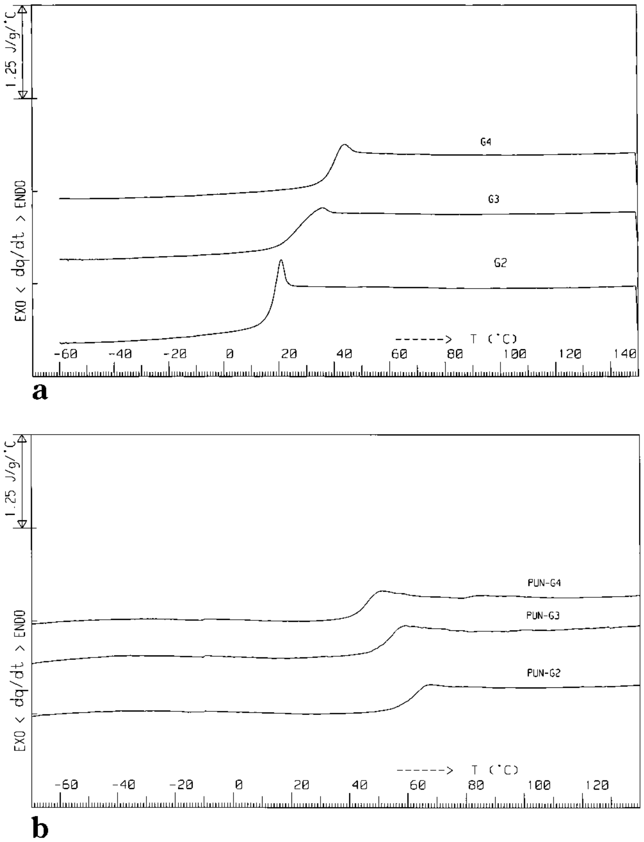

Figure 3. DSC traces of dendritic wedges (a) and corresponding polyurethane networks bearing dendritic wedges (b). The data represent the second heating run.

Table 1. Swelling Ratios, Gel Fractions, and the Glass Transition Temperatures (T_g) of Polyurethane Networks Bearing Dendritic Wedges Where T_g Values of the Corresponding Dendritic Wedges Are Also Indicated

code	T_g (°C)[a]	gel fraction (%)	swelling (%)[b]
PUN-G2	53.5 (17.8)	97	213
PUN-G3	47.9 (30.8)	94	232
PUN-G4	40.5 (37.9)	87	298

[a] The numbers between brackets are the T_g values of the corresponding dendritic wedges. [b] These are the swelling ratios of the gel fractions.

generations, which may act as a plasticizer. Owing to geometrical constraints, induced by dendritic side groups, the chemical reaction between hydroxyl and isocyanate groups is hampered especially for dendritic wedges of generation four. Hence, the resulting networks contain more defects as the generation number increases. Similar conclusions were drawn on the basis of our previous studies dealing with copolymerization of identical dendritic wedges with diisocyanates.[2] The lower cross-linking density for networks of higher generation may also be responsible for the decrease of T_g with generation number.

According to Flory, the equilibrium swelling of a Gaussian network is a function of molecular weights between two adjacent junction points (M_c) and the Flory–Huggins interaction parameter (χ).[6] The swelling behavior of the present polyurethane networks bearing dendritic wedges is different due to the following reasons. First of all, the Flory theory is developed for a Gaussian network, whereas the elastic chains in the present networks are too short to behave according to Gaussian statistics. The motion of these elastic chains may be further restricted by the presence of dendritic wedges contributing to the non-Gaussian behavior. In addition, for the present systems it is difficult to define M_c. The network chain between two cross-link points is in the middle chemically attached to a large dendritic wedge. It is possible that at least part of the dendritic wedge may contribute to the elastic nature of the network and so modifies the value of M_c.

The dendritic wedges, chemically attached to the polyurethane main chain, may be considered as a solvent, already present in the system. Therefore, the swelling ratio should decrease with increasing size of the dendritic wedges. As can be seen in Table 1, the reverse trend is actually observed, i.e., the degree of swelling increases with generation number. According to classical swelling theory,[1] such behavior is a direct consequence of a larger number of defects, which we have observed here for networks of higher generations. Alternatively, the increasing swelling ratio with dendrimer generation can be attributed to the possible ability of dendritic units to absorb solvent without changing the total volume.[7] Obviously in that case the mass swelling ratios, presented here, cannot be readily related to volumetric swelling ratios. Currently, we are investigating this phenomenon in more detail using NMR relaxation experiments.

B. Molecular Dynamics Simulations. To study the effect of dendritic wedges on swelling behavior in more detail, we have conducted molecular dynamics simulations. Owing to experimental restrictions, we decided to model only an idealized segment of the network as shown in Figure 4.

By changing the contribution of attractive and repulsive forces, we were able to calculate the radius of gyration (R_g) of simulated segments in both poor and good solvents. On the basis of these data, we could determine the volume of the system in solvents of different quality. The ratio of the volumes in poor and good solvents (V^{good}/V^{poor}) could be thought as a measure of the swelling behavior. In contrast to experimental swelling data, the ratio V^{good}/V^{poor} decreases with increasing generation number (see Table 2). It should be noted, however, that the experimental networks would not have the ability to expand as much as the limited modeling structures do.

A more reliable way of analyzing the modeling data is by determining the distance between two adjacent phosphorus atoms in the simulated segment of the polyurethane network. Because in a good solvent the structure is fully expanded, the calculated value is the maximum achievable distance. In a poor solvent, however, the structure is contracted and the distance between two neighboring phosphorus atoms decreases accordingly. Sterical effects induced by bulky dendritic wedges undoubtedly influence this decrease in distance. As can be seen in Table 2, the P–P distance in poor solvent is lowest for PUN-G2 and, considering statistical errors, comparable for PUN-G3 and PUN-G4. Apparently, even a P–P distance analysis is not able to unequivocally explain the experimental swelling results, and consequently more investigations are needed in this direction.

C. ^{31}P NMR. Since each junction point in the network contains a phosphorus atom, ^{31}P NMR is the method of choice to study the local mobility of network junctions and the effect of bulky dendritic groups. Figure 5 shows the ^{31}P NMR spectra of PUN-G2, PUN-G3, and PUN-

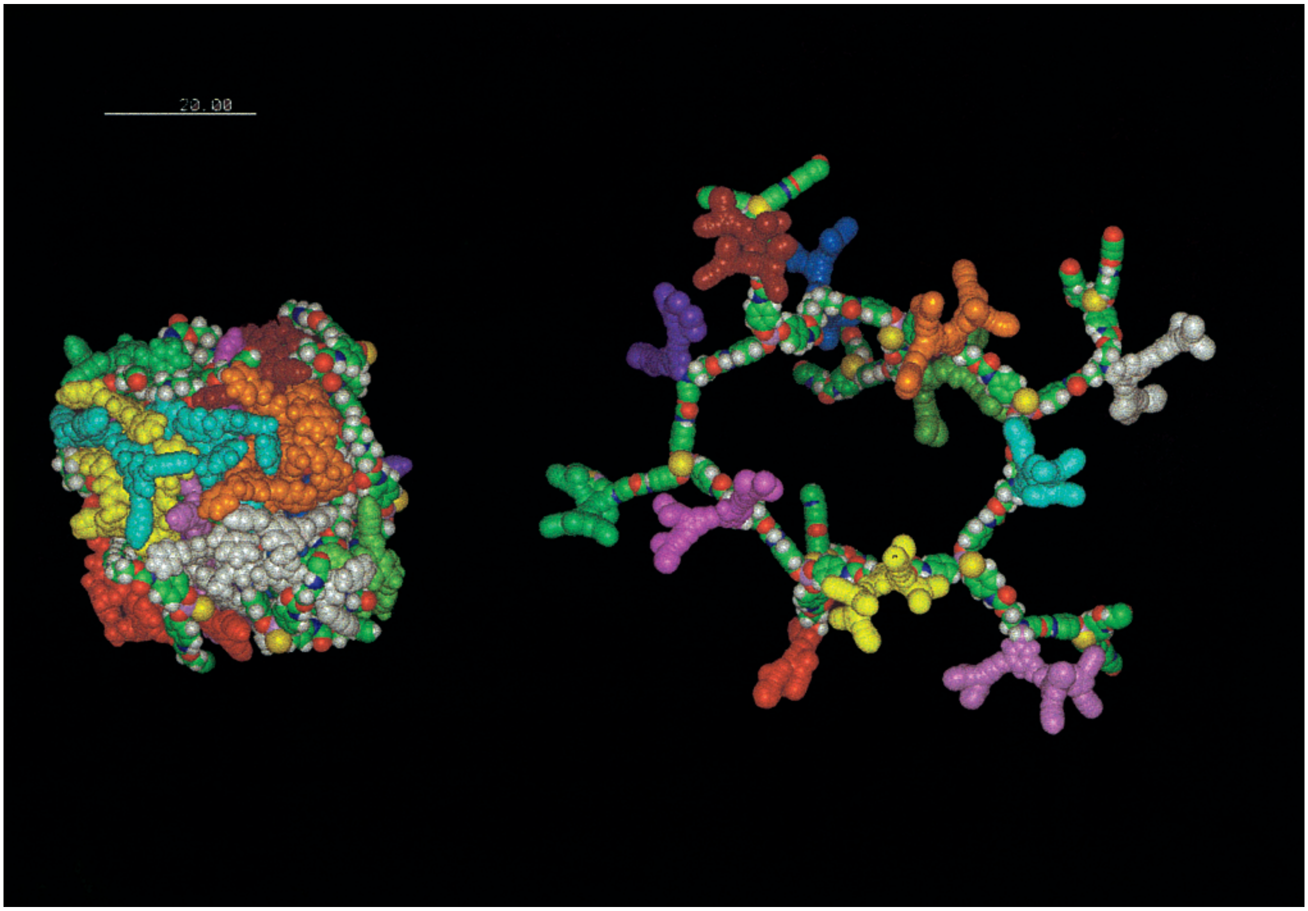

Figure 4. Average molecular configuration of a third-generation polyurethane network (PUN-G3) calculated from molecular dynamics simulations with a poor as well as a good solvent. To distinguish the various parts, the dendritic wedges are colored differently. The simulated structures contain six cross-link points. The average molecular configurations have no physical meaning and are computed from $\langle x_i \rangle = \sum_{j=1}^{n} x_{ij}$; $\langle y_i \rangle = \sum_{j=1}^{n} y_{ij}$; $\langle z_i \rangle = \sum_{j=1}^{n} z_{ij}$ with $\langle x_i \rangle$, $\langle y_i \rangle$, and $\langle z_i \rangle$ denoting the average x, average y, and average z position of atom "i", respectively, and n is the number of configurations in the trajectory being analyzed.

Table 2. Data Obtained from Molecular Dynamics Simulations of Dendritic Wedges and Polyurethane Networks

	R_g (Å)		V (Å^3)[a]		distance (Å)[b]		
code	poor	good	poor	good	poor	good	$V^{\text{good}}/V^{\text{poor}}$
G2	5.8 ± 0.3	7.6 ± 0.4	1760 ± 52	3960 ± 120			2.2
G3	6.7 ± 0.3	10.6 ± 0.6	2710 ± 70	10730 ± 350			4.0
G4	8.2 ± 0.1	14.2 ± 0.5	4970 ± 35	25810 ± 525			5.2
PUN-G2[c]	14.0	29.1	24 731	222 096	11.7 ± 3.7	20.8 ± 0.9	9.0
PUN-G3[c]	16.6	32.4	41 227	306 547	16.0 ± 5.2	21.6 ± 1.3	7.5
PUN-G4[c]	20.4	35.6	76 516	406 642	15.0 ± 2.5	22.5 ± 0.8	5.3

[a] V stands for volume calculated from $V = {}^4/_3\pi R^3$ where $R = (\sqrt{5/3})R_g$. [b] In each simulated structure, there are six phosphorus atoms. These values are the average distances, and the corresponding variations, between two adjacent phosphorus atoms. [c] The standard deviations for these systems were less than 0.1 Å.

G4 measured at different swelling stages. For dry samples, the line is very broad and reveals the usual powder pattern for axially symmetric chemical shift anisotropy.[8] A single symmetric line is observed in swollen samples. The line width decreases significantly upon swelling and reaches a plateau value with increasing swelling ratio. The line widths as a function of the swelling ratio are shown in Figure 6. When comparing PUN-G2 with PUN-G3, the line width for networks of generation three appears to be slightly larger at equal swelling ratios, and the line narrows at slightly higher solvent content values. This is the direct consequence of the restrictions of the mobility induced by larger dendritic wedges. The accuracy of NMR measurements for PUN-G4 was low because of the relatively small concentration of phosphorus atoms. As a result the line width data are highly scattered, making the interpretation of the data difficult. The above results are supported by spin−lattice (T_1) relaxation experiments, conducted on the networks at a swelling ratio of 100%. This solvent content is slightly higher than the solvent concentration for which the line narrowing is observed. At such solvent content, the frequency of junction point motion is expected to be less than the resonance frequency of ^{31}P, i.e., 162 MHz. In this case a decrease in molecular mobility causes an increase in ^{31}P T_1.[8] As can be seen in Figure 7, T_1 increases with generation number, indicating that the local mobility of the junction points is indeed limited by bulky dendritic wedges.

IV. Conclusions

We have shown that polyurethane networks bearing bulky groups can be prepared by polymerizing dendritic diols of various generations with a commercial triiso-

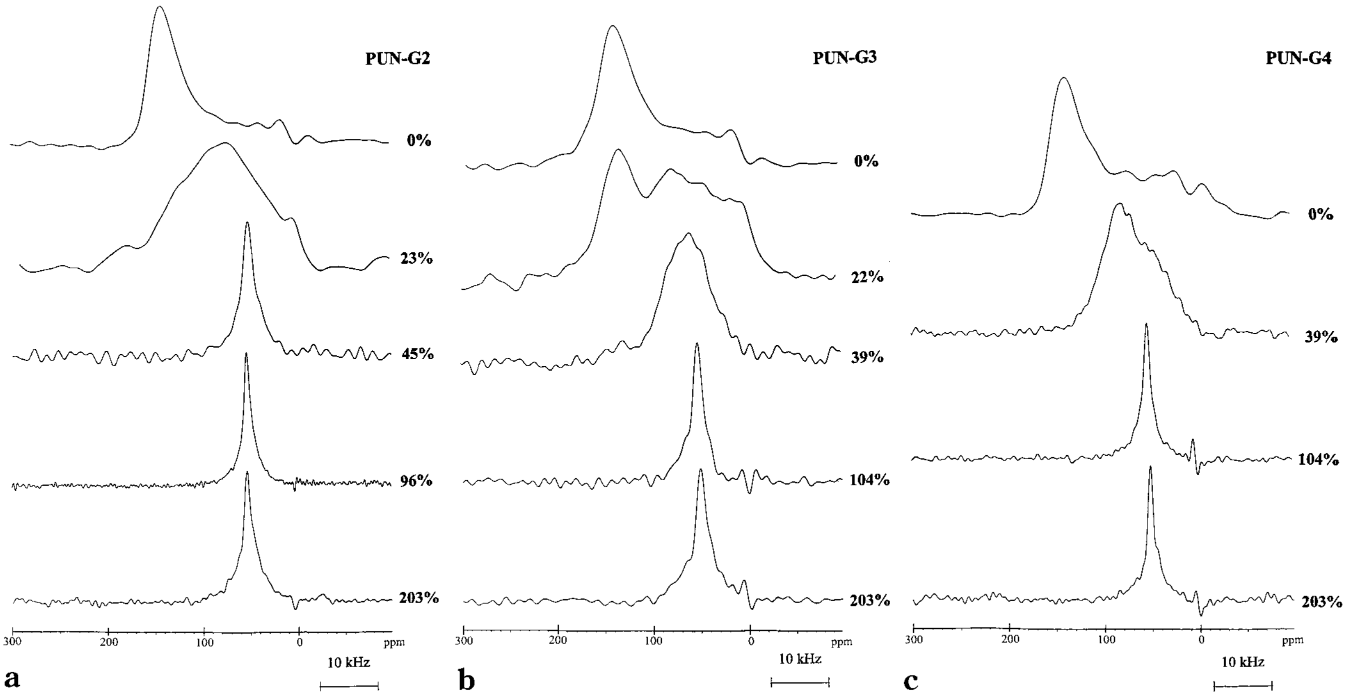

Figure 5. ^{31}P NMR spectra of polyurethane networks of different generations measured at different degrees of swelling: (a) PUN-G2; (b) PUN-G3; (c) PUN-G4.

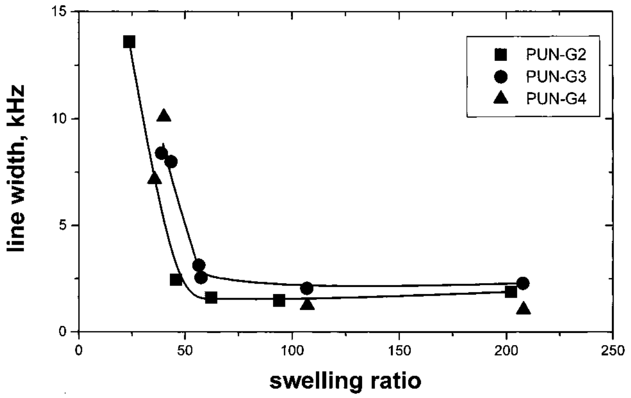

Figure 6. Line widths of ^{31}P NMR spectra plotted as a function of swelling ratio for polyurethane networks of various generations. The data for the polyurethane network bearing dendritic wedges of generation four (PUN-G4) are somewhat scattered due to the relatively low concentration of phosphorus. Therefore, no line is drawn through the data points measured for PUN-G4.

cyanate (Desmodur RFE). Owing to shielding effect of large dendritic wedges, the reaction between hydroxyl and isocyanate groups cannot be driven to completion, in particular in the case of dendritic wedges of generation four. Hence, the amount of gel fraction decreases with increasing generation number. In principle, the swelling ratio should decrease as a function of generation number, an assumption that is supported by molecular modeling calculations. For the experimental swelling ratios, however, the reverse trend was observed. These results were attributed to a larger number of defects for networks of higher generations. Finally, ^{31}P NMR (relaxation) experiments revealed unequivocally that the mobility of junction points decreases with generation number. This phenomenon will undoubtedly affect the mechanical properties of the polyurethane networks covered in the present study, which observation will be the subject of future publications.

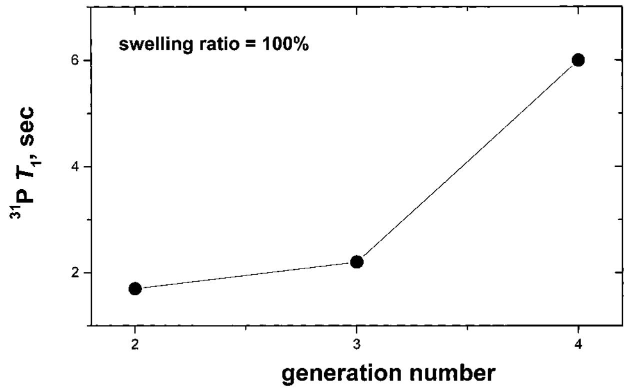

Figure 7. Spin-lattice (T_1) relaxation values for polyurethane networks of different generations with a swelling ratio of 100%.

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