Macromolecules **1997,** *30,* 5345−5351

Rigid Random Coils: Rotationally Confined Chain Molecules

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Received March 6, 1997; Revised Manuscript Received June 23, 1997[⊗]

ABSTRACT: Considered are chain molecules characterized by rotational potentials with a set of low energy states separated by large energy barriers. The expectation is that such chain molecules should exhibit unique properties. Polynorbornene and laterally substituted polynorbornenes are characteristic examples. Simulations based on ab initio methods, semiempirical quantum mechanical methods, and force field methods are employed in order to derive information on the chain conformation and dynamics of the polynorbornenes. The finding is that they display a random rigid coil with a characteristic ratio of the order of 10, that they are not able to collapse even in poor solvents, and that isolated chains are rigid up to temperatures well above room temperature. Details of the rotational potential can be controlled by a proper selection of lateral substituents.

I. Introduction

The chain conformation and the flexibility of the chain molecule are key factors which control solution properties, structure formation, and dynamics in the condensed state as well as macroscopic properties. Rigid or semiflexible rodlike chain molecules, for instance, are known to display lyotropic phases or liquid crystalline melts with unusual flow properties and solid states characterized, for instance, by peculiar mechanical properties.[1−3] Flexible chain molecules with coillike conformations, on the other hand, exhibit rheological properties in solutions and melts which are controlled by the formation of entanglements and disentanglement processes.[4−6] Their solubility in low molar mass solvents as well as in polymers is strongly enhanced relative to the one characteristic of rigid rodlike polymers. Permeation properties, diffusion, and dielectric and dynamical mechanical properties are further examples of properties which depend on the chain conformation and the chain flexibility.[7,8] It is obvious that materials with novel properties will result if we succeed in constructing chain molecules which assume a coillike conformation yet are rigid even at elevated temperatures.

To achieve this we have to focus on chain molecules with unique rotational potentials. First of all, the torsional angles corresponding to the energy minima of the potential have to be distributed in such a way such that nonextended random chain conformations result. Second, the rotational potential should be characterized by the presence of very large activation barriers, which reduce the probability of jumps across the barrier in ideal cases effectively to zero. We envision unique properties for such materials both in the melt and in solution.

The chain molecules should in ideal cases neither swell or collapse to a significant degree even if the quality of the solvent changes strongly.

The chain conformation will be only weakly modified in the presence of flow fields, disentanglement effects will be strongly reduced so that the properties of the condensed state should correspond to that of a thermoset, yet the material should be soluble since it has, in principle, the same chain statistics as a flexible chain.

We expect unusual diffusion and barrier properties due to the absence of reptation processes and other molecular motions giving rise to large displacements.

An interesting feature of such chain molecules could be that the population of the low-energy states does not depend on the temperature but is fixed during the polymerization process. Real systems will, of course, be characterized by small angular fluctuations within a single conformer state.[9] However, we expect these effects to be small (see experimental results on chain conformations in different solvents).

Chain molecules constructed in this way should furthermore exhibit unique dynamical properties if the height of the energy barrier is selected appropriately. The chain will be able to perform rotational motions at elevated temperatures, yet the number of conformational changes per unit time will be small. We may envision the case that—on cooling—the time required for one conformational step accross a barrier becomes in a specific temperature range longer than the time of observation. This would correspond to the freezing-in of a single chain for instance in solution. De Gennes[10] has proposed for this reason the term *single chain glass* for such a situation. A proper choice of the heights of the energy barriers would allow to select the temperature at which this freezing-in happens more or less at will, in any case also in a temperature range well above room temperature.

It is our aim to synthesize such chain molecules and to characterize their properties. This contribution is concerned predominantly with simulations of such rotationally constrained chain molecules. The intention is to gain information on appropriate chain structures. We decided to take the polynorbornene as the starting structure for the chain backbone since polynorbornene obviously possesses features characteristic of such rotationally hindered chain molecules, as recently pointed out by us.[11] In the next step we consider polynorbornenes modified by the introduction of bulky lateral groups.The expectation is that these substitutions lead to additional contraints on the rotational degrees of freedom.

II. Simulation Methods

In order to get an insight into the chain conformation, dynamics, and rigidity, we performed atomistic simulations of the unmodified polynorbornene and polynor-

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

S0024-9297(97)00306-9 CCC: $14.00

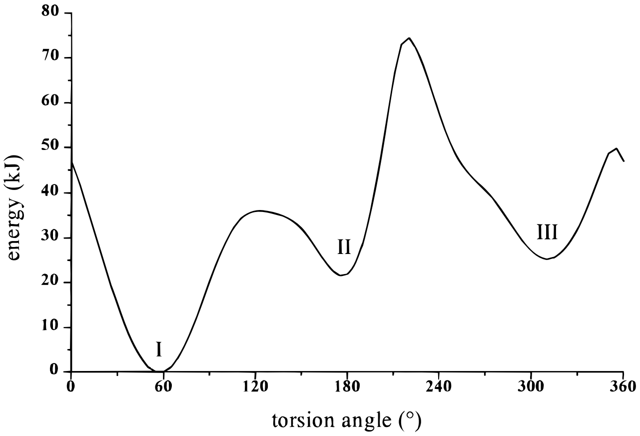

Figure 1. One-dimensional rotational potential of polynorbornene.

bornenes with lateral groups. Polymer chain dynamics including the transition into the collapsed state have been investigated successfully on the basis of computer simulations.[12−19] We will consider isolated chains in vacuum which corresponds to the case of a poor solvent with a low viscosity.[19] Semiempirical quantum mechanical calculations were performed using the MOPAC software package,[20] in particular the Austin Model 1 (AM1)[21] and the Parametric Model 3 (PM3)[22] implemented on SGI Indy and IBM RS/6000 computers.

The program Cerius2 of Molecular Simulations Inc.[23] was chosen to carry out the molecular dynamics simulations. For all molecular dynamics simulations we selected an all atom approach including charges, and we used the DREIDING force field by Goddard et al.[24] In order to study neighbor effects on the central bond we built single chain structures containing 12 monomer units. The simulation time for each system was 50 ps.

III. Results and Discussions

III.1. Unsubstituted Polynorbornene. One-Dimensional Rotational Potential. The rotational potential of unsubstituted polynorbornene was recently calculated by us based with ab initio quantum mechanical methods.[11] We will use in the following the force field approach since we intend to calculate the properties of larger chain molecules. Yet the rotational potential obtained from the force field reflects the major features of the one obtained by ab initio calculations quite closely. It is displayed in Figure 1. It is characterized by three energy minima. The conformational state with the lowest energy which we will call I in the following is located at a torsional angle of about $\phi = 60°$. The two other minima occur at torsional angles of 175 (II) and 315° (III), respectively and the corresponding energy differences relative to the lowest energy state amount to 19 and 24 kJ/mol, respectively. It is obvious that the chain conformation is controlled in a broad temperature range extending well above room temperature by a nearly complete occupation of the lowest energy state. The ratio of the population numbers is on the order of 10^{-4} in the temperature range mentioned above. The barrier heights amount to 35 and 50 kJ/mol, respectively, which allows motions only at elevated temperatures.

The low-energy conformation does not correspond, however, to an extended state as it would be in the case of polyethylene due to the minima I, II, and III of the rotational potential. In fact, using the rotational isomeric state approach[24] for these conformer states we calculated for polynorbornene a characteristic ratio

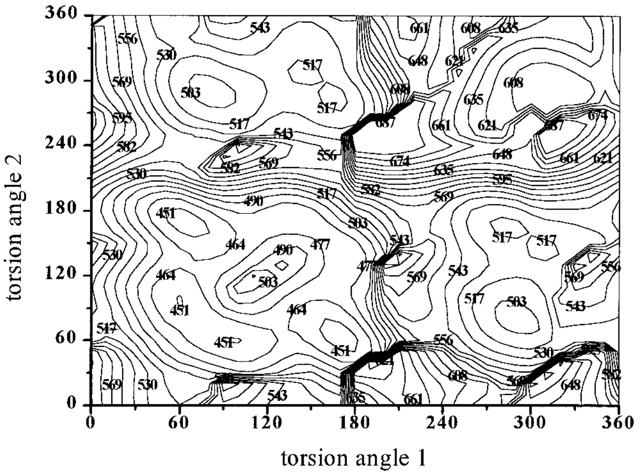

Figure 2. Two-dimensional rotational potential of the polynorbornene.

$$C_n = \langle r^2 \rangle / n l^2$$

of 12.1 (where $\langle r^2 \rangle$ is the mean square value of the end-to-end vector). The value derived from light scattering experiments,[26] on the other hand, turned out to be on the order of 11.

Taking the magnitude of the rotational energy barriers given above also into account we have to conclude that polynorbornene is rigid at lower temperature and nevertheless assumes a randomly coiled state. Note that similar values of the characteristic ratio have been reported for chain molecules such as polystyrene[27,28] and poly(vinyl chloride)[19] which, in fact, are semiflexible and may assume at room temperature in solution or in the isolated state a large number of different conformations.

Two-Dimensional Rotational Potential. The disadvantage of the analysis of the one-dimensional rotational potential performed so far is that it does not properly take into account neighboring effects. Yet, these are known to affect the chain conformation even in the case of highly flexible nonbulky polymers. Information on the effect of neighbors is available to a first approximation from a consideration of the two-dimensional rotational potential. Figure 2 displays this potential for the case of polynorbornene. Each contour map was created stepwise by rotating the two connecting bonds, minimizing the remaining structure under the consideration of charges. The calculated potential energy surfaces consist of 1369 points.

The two-dimensional rotational potential is characterized by a minimum corresponding to combinations of the rotational states I and II. The prediction is that a second low-energy state with about the same energy occurrs for combinations of rotational state with torsions angles of 60 and 100°, respectively. The barrier between these two low-energy states amounts to about 16 kJ/mol. We observe furthermore two local energy minima, the population probabilities of which are, however, very small at room temperature. The chain conformation is thus predominantly controlled by the sequences I/II and 60 and 100°, respectively, and the dynamics by the energy barrier of about 16 kJ/mol between them.

Figure 3 represents the result of molecular dynamics calculations performed on isolated chain molecules. The observation is that the chain becomes less extended with increasing computation time yet does not collapse: the

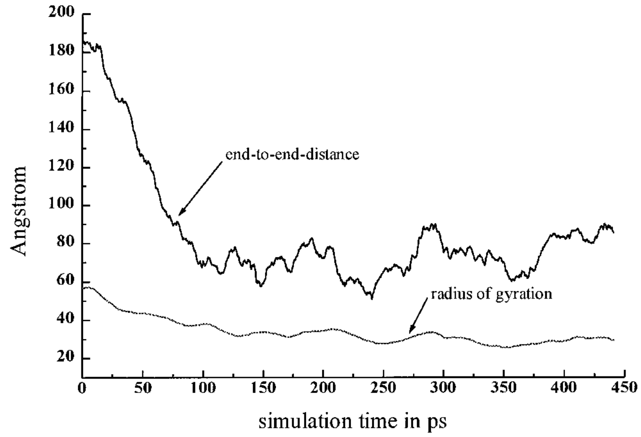

Figure 3. Results of molecular dynamics simulations performed on a polynorbornene chain with 100 monomer units.

polynorbornene chain approaches limiting values both for the end-to-end distance and the radius of gyration, which deviate strongly from those in the collapsed state. It is instructive to compare the behavior of polynorbornene with the behavior of the semiflexible polymer poly (vinyl chloride).

Tanaka and Mattice[19] performed detailed simulations on isolated PVC chains in vacuum. They found that the PVC chains collapse approaching a characteristic ratio which deviates strongly from the one of the unperturbed state and is close to the one expected for the collapsed state. Similar results were obtained for the ratio of the square of the end-to-end distance and the radius of gyration. Our simulation on polynorbornene led to characteristic ratio C_n on the order of 8.5, which is thus smaller than the values obtained from the RIS calculations and from experiments in solution. One reason for the somewhat smaller value of the characteristic ratio obtained in the simulations certainly is that the vacuum has to be considered as a poor solvent; a second is that other low-energy states control the actual chain conformation.

The ratio of the square of the end-to-end distance and the radius of gyration was found to fluctuate about a value of 5.5, which is thus close to the value expected for an unperturbed chain conformation. Both results clearly point out that the chain is rigid and unable to collapse and that it displays a nearly unperturbed state. Finally we point out that the chain rigidity is also apparent from the magnitude of the fluctuation of the end-to-end distance. It is on the order of 20% for the polynorbornene as compared to about 50% reported for poly(vinyl chloride).

Torsional Angle Distribution. On the basis of the results reported above, we conclude that the pseudo-three-dimensional structure of the monomer strongly influences the conformational space. The expectation is that this effect is not only limited to the nearest neighbors. We therefore decided to analyze the influence of a larger number of neighboring monomers on a central bond including all effects that are caused by complex steric and electronic interactions. To achieve this goal we performed molecular dynamics simulations on polymer chains consisting of 12 monomers. These chains were built from preminimized trimeric structures, and the complete chains containing 12 monomers were subsequently minimized using the conjugate gradient algorithm. All molecular dynamics simulations were performed for 200 ps and included charges. In order to get an insight into the local chain dynamics of internal bonds, we selected a particular bond and studied the evolution of the torsional angle vs time for different temperatures.

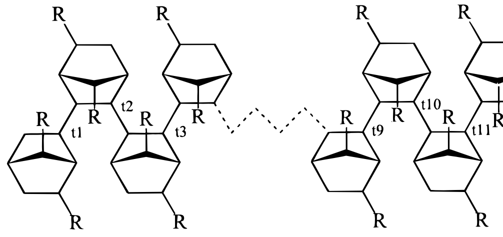

Figure 4. Numbering of the torsions t1−t11.

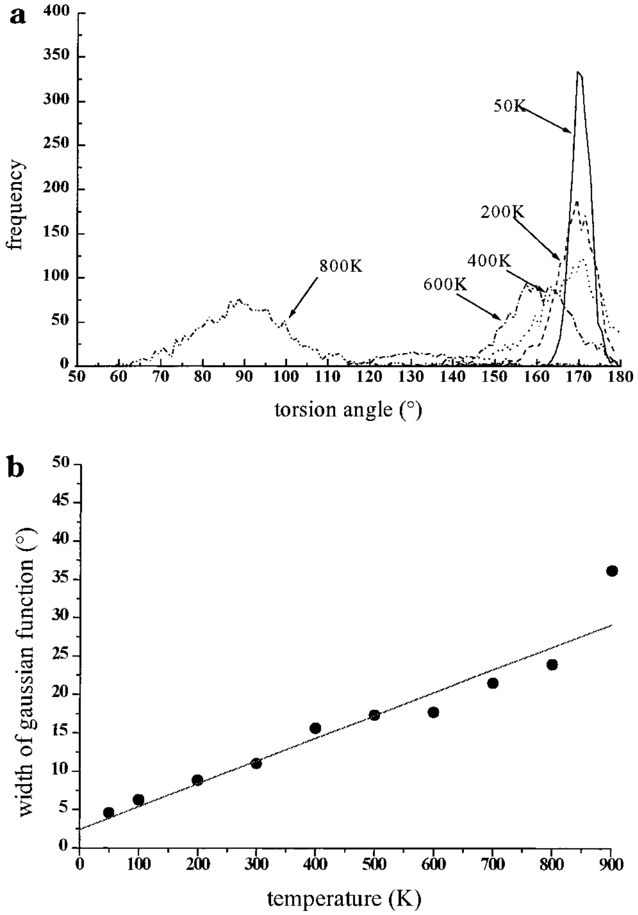

Figure 5. (a) Distribution function for the torsional angles of the central bond at various temperatures for polynorbornene. (b) Dependence of the half-width on the temperature.

We found significant fluctuations of the terminal torsion angles torsions t1 and t11, which is not surprising and is not very significant. More important is the behavior of the central torsion connecting the monomers 6 and 7. This torsion samples the influence of five neighbors on both side of the selected bond, and we assume that this model will represent all sterical effects on the particular torsion which can be found in much longer chains.The results are shown in Figure 5a.

The central torsional angle is characterized at low temperatures by a narrow distribution. The distribution gets significantly broader, and the average value shifts slightly with increasing temperature. These results seem to indicate that the torsional angles of the central bond remain within the same multidimensional low-energy state; i.e., no jumps occurr about energy barriers leading to other low-energy states. We were able to fit the distribution to a Gaussian distribution, and we evaluated the half-width as a function of the

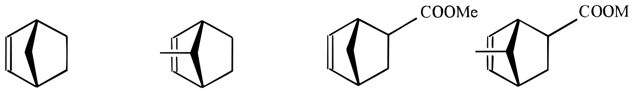

Figure 6. Polynorbornenes with lateral substituents.

temperature. The results are shown in Figure 5b. The half-width is found to increase linearly with increasing temperature. It is on the order of 5° at 50 K and assumes a value of about 25° at 800 K.

The linear increase predicted from the simulations is of considerable interest. The mean square value of a fluctuating quantity is known from statistical mechanics to be proportional to the square of the half-width of the corresponding Gaussian distribution.[29] On the basis of our results for the computer simulations, we therefore have to conclude that the fluctuations of the torsional angle increase proportional to the square of the temperature. Assuming, on the other hand, that the fluctuations are controlled by thermal agitations within a constant low-energy torsional state with a given curvature of the potential, we expect that the mean square value increases linearly with the temperature. We therefore conclude that the multidimensional rotational potential itself is subjected to fluctuations resulting from fluctuations of the location of all the monomer units along the chain.

Figure 5a reveals an interesting feature: a second range of torsional angles becomes populated for temperatures above approximately 800 K. This has to be taken as an indication for the onset of rotational jumps across barriers. First indications for the onset of free rotations appear at 1600 K. (This value has, of course, no realistic meaning because of the decomposition temperature of polynorbornene at about 600 K.)

It is instructive to compare these results with the ones obtained for the experimentally well-characterized semiflexible polystyrene. Polystyrene is found from our simulations to display a broad range of torsional angles already at temperatures as low as 50 K and to perform free rotations about the central single bond already at temperatures of the order of 300 K. Again this comparison cleary points out the strong rotational confinement of the polynorbornene.

III.2. Laterally Substituted Polynorbornenes. One-Dimensional Rotational Potential. The laterally substituted polynorbornenes analyzed in this contribution are shown in Figure 6. We consider methyl-substituted polynorbornene (7-MEPN), methyl ester substituted (PNMeEster) and finally methyl methyl ester substituted polynorbornene (7-MePNMeEster). To start with we will compare the one-dimensional rotational potentials of the substituted polynorbornenes with the one of the unsubstituted PN.

The methyl-substituted PN is characterized by just one low-energy conformation located at a torsional angle of slightly below 60° similar to the case of the unsubstituted PN (Figure 7). The curvature responsible for torsional fluctuations at elevated temperatures are about equal in both cases. The methyl-substituted PN displays no other low energy state conformation in contrast to the unsubstituted PN. The energy barrier is on the order of 110 kJ/mol and thus is significantly higher than the ones found for PN. We thus have to conclude that the methyl substitution causes the chain molecules to become even more rigid than the unmodified polynorbornene. Very similar results were obtained from semiempirical quantum mechanical calculations, and this holds as well for the rotational potentials of the other modified polynorbornenes considered in the following.

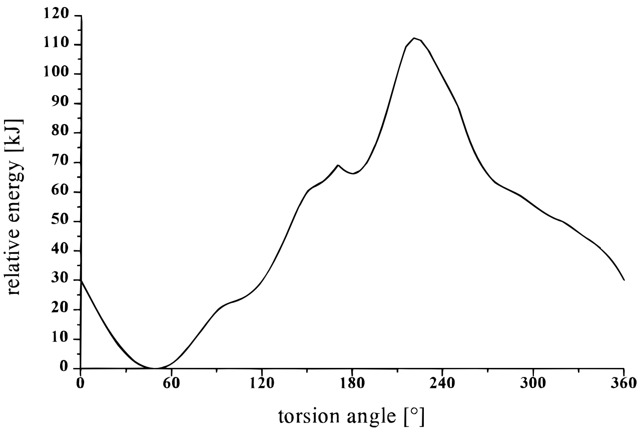

Figure 7. One-dimensional rotational potential of methyl-substituted polynorbornene.

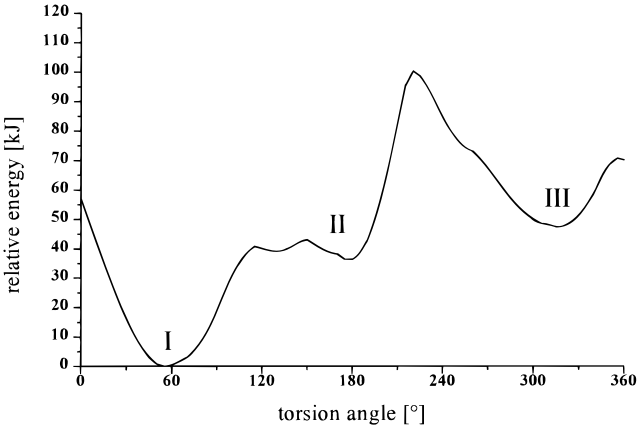

Figure 8. One-dimensional rotational potential of methyl ester substituted polynorbornene.

The methyl ester substitution gives rise to a rotational potential which roughly resembles the one of the unmodified PN (Figure 8). We observe three low energy conformations at roughly 60° (I), 180° (II), and 320° (III). There is only a small energy barrier between the rotational isomeric states I and II, yet the absolute energy of state II compared to state I is on the order of 37 kJ/mol and is thus larger by a factor of about 2 compared with the PN. The conformational state III is characterized by an even higher energy amounting to about 50 kJ/mol and the rotational barriers characterizing the transition II/III and III/I are about 100 and 60 kJ/mol and thus also significantly larger than in the case of PN. The methyl ester substitution thus makes the chain stiffer compared to the unmodified PN, yet it does not restrict the rotational states as strongly as the methyl substitution.

Finally we consider the combined substitution methyl and methyl ester (Figure 9). It is obvious that the rotational potential resembles that of the methyl substitution to a first approximation. The curvature characteristic of the low-energy state is modified in the sense that it is weaker for the combined substitution and that a weak second low-energy state is formed close to the lowest one. The magnitude of the energy barrier is unchanged.

We thus have to conclude that the methyl substitution has the strongest effect on the rotational potential. It gives rise to an annihilation of two higher rotational isomeric states and to an increase of the rotational barrier.

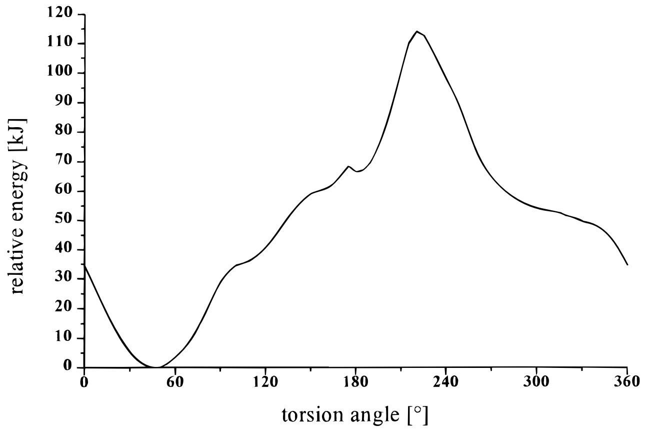

Figure 9. One-dimensional rotational potential of the methyl methyl ester substituted polynorbornene.

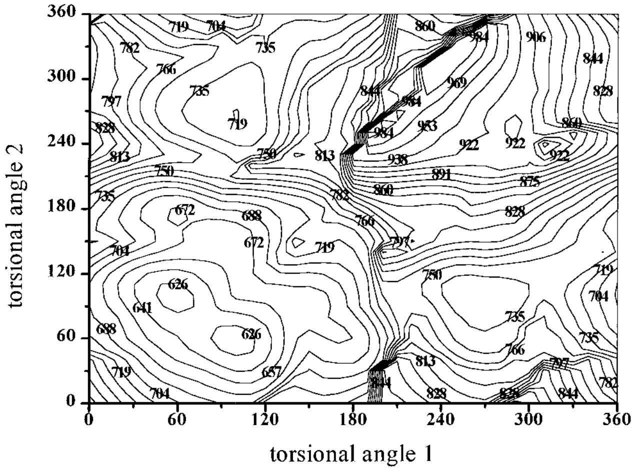

Figure 10. Two-dimensional rotational potential of the methyl methyl ester substituted polynorbornene.

Two-Dimensional Rotational Potential. We will concentrate in the following on the methyl methyl ester substituted polynorbornene (7-MePNMeEster). Its two-dimensional rotational potential is displayed in Figure 10. The combination of the states I and II no longer leads to an energy minimum as in the case of the unsubstituted polynorbornene. The rotational potential is characterized by a low-energy state corresponding to a combination of rotational state with the torsion angles amounting to 60 and 100°, respectively. The other local minimum has an energy which is approximately 90 kJ/mol larger than the one of the absolute minimum. The activation barrier amounts to about 125 kJ/mol. We thus have to conclude that the chain conformation is completely controlled by the one low-energy rotational state and that the chain molecule is significantly stiffer compared to the already stiff polynorbonene.

Molecular dynamics simulations (Figure 11) show that the chain molecule assumes a rigid random coil conformation with a characteristic ratio on the order of 7.5. Isolated chains in vacuum do not collapse, and the fluctuations of the radius of gyration are small compared with those reported for PVC. The ratio of the square of the end-to-end distance and the radius of gyration was found to fluctuate between 11.4 and 7.6 with an average value of 9.6, deviating from the value expected for an unperturbed chain conformation. Rods would be characterized by a value of 12. It seems that one reason is that the number of chain units was quite small—100 in this case.

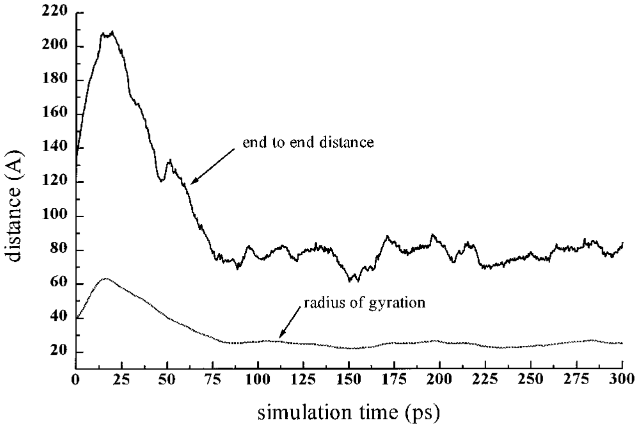

Figure 11. Results of molecular dynamics simulations performed on a methyl methyl ester substituted polynorbornene.

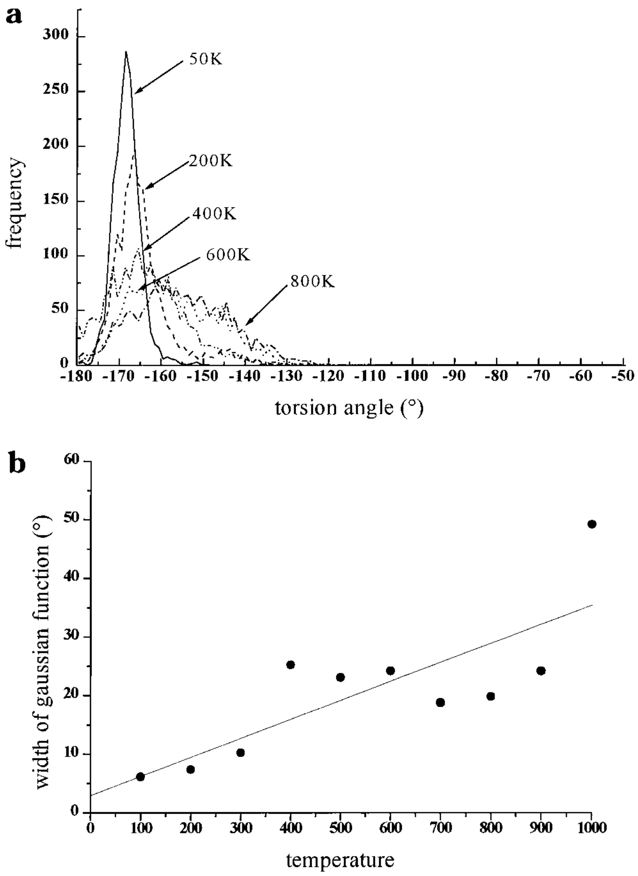

Figure 12. (a) Distribution function for the torsional angles of the central bond at various temperatures for the methyl methyl ester substituted polynorbornene. (b) dependence of the half-width on the temperature.

Torsional Angle Distribution. Figure 12a displays the torsional angle distribution obtained for the central bond of a chain consisting of 12 monomer units of the substituted polynorbornene. Details were given above. The observation is as in the case of the unsubstituted polynorbornene that the central torsional angle is characterized by a narrow distribution with a half-width increasing linearly with temperature as in the case of the unsubstituted polynorbornene. The increase is, however, in the same range as in the case of PN (Figure 12b). The temperatures at which a second range of torsional angles becomes populated and at which first indications for the onset of free rotations about the central single bond appear, respectively, are significantly larger—they amount to 1000 and 2000 K—than

Table 1. Ratio of the Radius of Gyration and the Hydrodynamic Radius as Obtained from Light Scattering

Dynamical light scattering

M_W	$\sigma = R_g/R_h$
65 400	1.68
255 000	1.47
351 000	1.50
433 000	1.47

Theoretical values for ideal geometries

shape	$\sigma = R_g/R_h$
collapsed coil	0.75
gaussian coil	1.50
rigid rod	2.00

the one characteristic of the unmodified polynorbornene. Both findings have to be taken as indications for the stronger confinement of the torsions for the laterally substituted polynorbornene.

IV. Simulations and Experiments: A Comparison

The simulations lead to the following conclusions. Polynorbornene and in particular polynorbornenes with bulky lateral substituents are definitely examples of rotationally confined chain molecules. They display a random coil conformation, yet they are rigid and cannot collapse. Experimental results obtained on polynorbornene in solutions agree with these conclusions.

Chain Conformation. Light scattering studies lead to a characteristic ratio of 11 which is close to the values obtained from computer simulations.

The Mark Houwink constant which is experimentally observed for a solution of PN in cyclohexane as well as chlorobenzene amounted to 0.56 which indicates only a slight deviation from the unperturbed state.[30] This holds despite the fact that the solubility parameters of the two solvents differ significantly (cyclohexane, 8.2 $(\mathrm{cal/cm^3})^{1/2}$; chlorobenzene, 9.5 $(\mathrm{cal/cm^3})^{1/2}$).

Static and dynamic light scattering investigations[30] gave ratios σ of the radius of gyration and the hydrodynamic radius which are close to 1.5 the value expected for an ideal Gaussian coil (see Table 1).

Chain Dynamics. The simulations show that the dynamics of the chain molecules are controlled by large energy barriers. The temperatures at which the low-temperature narrow distribution of the torsional angle is significantly broadened and at which a certain degree of mobility exists are larger by about 400−500 K compared with those for polystyrene, for example. It is quite obvious that the polystyrene chains are highly mobile at those temperatures at which the glass transition occurs in the condensed state, i.e. about 380 K; an isolated chain is able to perform free rotations at this temperature. The polynorbornene chain, on the other hand, is rotationally strongly confined at a temperature of about 500 K at which it displays a glass transition in the condensed state.

These differences in the chain mobility should show up in the properties of the melt. In fact, the thermal mechanical analysis (TMA) gave a surprising result as is apparent from Figure 13. The test pin which is loaded is not able to penetrate significantly into the bulk material at the glass transition temperature, which amounts to 493 K, as is apparent from DSC studies and small-angle X-ray results as well as from extrapolations on copolymers.[26] The penetration is only very weak and gets significantly larger only at temperatures above 600 K. Similar experiments performed on flexible or semiflexibe chain molecules lead, on the other hand, to a good agreement between the TMA data and DSC data, for instance. We conclude that the results obtained for PN indicate the rigid nature of the chains at the glass transition temperature. The beginning of decomposition is the origin of the penetration at higher temperatures as apparent from TGA studies. We would like to point out that preliminary NMR investigations show the absence of significant molecular motions up to temperatures of about 373 K.[31]

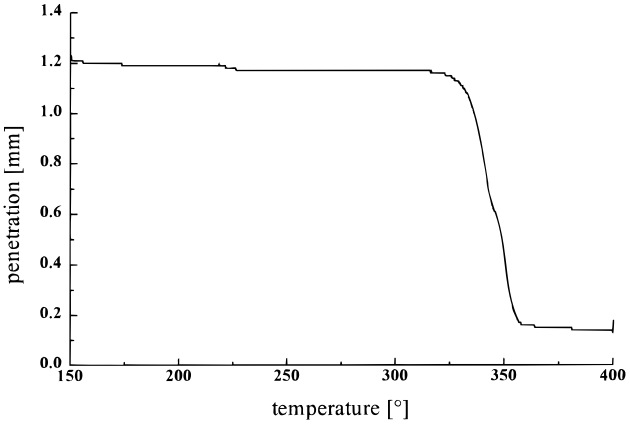

Figure 13. Thermal mechanical response curve obtained for polynorbornene.

Finally we adress the problem of the glass transition of the single isolated chain in the spirit of the suggestion by de Gennes.[10] Unfortunatelly there seems to be no unique way of extracting a glass transition temperature. Taking the temperature at which the chain begins to occupy a second range of torsional angles as a measure of the glass transition of a single chain, we obtain the following values: polystyrene, 200 K; PN, 800 K; and the substituted PN, 1000 K, respectively. These are obviously not related to the glass transition temperatures experienced in the condensed state, yet these values manifest the strong differences in mobility of the different chain molecules.

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MA970306Z