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Study of Sol Extraction from Model Poly(dimethylsiloxane) Networks Using Pulsed Gradient Nuclear Magnetic Resonance Diffusion Measurements†

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ABSTRACT: Model poly(dimethylsiloxane) (PDMS) networks have been prepared from a blend of hydroxyl-terminated molecules of two sizes, 85 mol % M_n = 550 and 15 mol % M_n = 18 000, using tetraethoxysilane as cross-linking agent at stoichiometric concentration in the presence of a catalyst. Sol was extracted for various lengths of time by swelling in toluene; up to 4.2% of sample weight was extractable in 5 days. The progress of extraction was followed by measuring NMR relaxation and diffusion of sol molecules in the unswelled network, using the pulsed-gradient spin-echo method. The smaller, faster diffusing sol molecules were extracted in <1 h, while the largest molecules required days to extract. There was evidence that the largest sol molecules are entangled with the network. Results suggest that prolonged extraction is required for PDMS networks destined as host materials for the study of the kinetics of polymeric trace additives.

I. Introduction

The use and study of model elastomeric networks have witnessed a tremendous popularity during the past 15 years.[1] The ability of dealing with a well-controlled and well-characterized network confers obvious advantages when it comes to verifying the various theories of rubberlike elasticity and developing new characterization techniques to test and evaluate cross-linked structures.[2–4]

The widespread attention enjoyed by these model networks dictates a most careful study of the preparation reactions employed to synthesize them and a close, critical look at the techniques used to assess the model character of the networks. It becomes immediately apparent that this information is indispensable, and any well-founded data about the conditions and the structure of the model networks can be invaluable.

Poly(dimethylsiloxane) (PDMS) is a class of semiinorganic polymers that has attracted the attention of polymer scientists for a long time. Model networks prepared from PDMS chains have been the subject of careful studies during the past.[3–6] Particular attention has been directed toward difunctional chains with various reactive groups. Vinyl-terminated as well as hydroxyl-terminated chains have been used to prepare networks of varying functionality.[3–6] A number of publications have been devoted to the subject of studying the reaction pathways and the possible byproducts generated from these synthetic procedures.[7–9]

The present work focuses on the extraction process, the step following the synthesis of the network, necessary in order to remove the unreactive soluble material from the network. It is also a way to assess the extent of the cross-linking reaction itself. The soluble fraction (sol) can vary between 1 and 4 wt % for these model networks, with a value of 2 wt % being typical.

Inefficient extraction of the sol is undesirable, since the physical properties of the network are affected by its presence. We study the efficiency of the extraction process by using pulsed-gradient spin-echo NMR, a technique well suited for the study of diffusion processes in polymers.[10]

By employing the concept of model networks, it is possible to prepare networks with unusual architectures and properties. One type of these networks is the so-called "bimodal" network.[11] In contrast to the "unimodal" network, where chains with only one molecular weight are employed, bimodal networks possess a bimodal distribution of network chains (i.e., short and long chains). Recent studies of this type of network have documented their unusual mechanical,[11,12] swelling,[12–14] and optical[15] behavior. In the present study we focus our attention on bimodal PDMS networks with a composition of 85 mol % in short chains.

II. Experimental Section

A. Synthesis of Networks. The polycondensation reaction was carried out in the bulk using α,ω-dihydroxypoly(dimethylsiloxane) (repeat unit $-[Si(CH_3)_2O]-$). Hydroxyl-terminated polymers were chosen because of the apparent simplicity of the reaction. The only byproduct is volatile ethanol. The molecular weight of the polymers was 550 g for the short chains and 18 000 g for the long chains, the latter being somewhat polydisperse. The amount of the short chains in the network amounted to 85 mol %. The catalyst used was stannous 2-ethyl hexanoate, and the cross-linking agent was tetraethoxysilane, $Si(OEt)_4$. All chemicals were purchased from Petrarch, Inc. The reaction scheme is

$$-[Si(CH_3)_2O]- + Si(OEt)_4 \rightarrow \text{network} + EtOH \qquad (1)$$

The short and long chains were mixed thoroughly and degassed for ca. 1 h before the cross-linker was added. The cross-linking agent was present in the amounts required to give exact stoichiometric balance between ethoxy groups and the hydroxyl groups in the PDMS mixture. The catalyst was present in the amount corresponding to ca. 1% by weight of the polymer.

The reaction batch was thoroughly mixed, poured into a Teflon-covered glass mold of dimensions 5 × 3 × 0.1 cm, and put under a partial N_2 atmosphere at room temperature for a period of 3 days. The mixture had solidified after 2 days.

B. Extraction. The resulting networks were carefully removed from the mold and cut in sheets of dimensions 1 × 2

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Table I
Extraction Details

extraction time	V_{2c},[a] %
15 min	2.82 ± 0.06
30 min	2.69 ± 0.05
60 min	4.12 ± 0.08
90 min	3.93 ± 0.08
5 days	4.21 ± 0.08

[a] Sol fraction.

cm. They were extracted in toluene for various amounts of time, between 15 min and 5 days. After the end of the swelling period, the strips were deswollen in methanol, a nonsolvent for PDMS.

The amount of sol was determined from the weight difference of the network before and after the swelling. Table I gives the necessary analytical results of the extraction process on all the samples. It is seen that the sol fraction varies as a function of extraction time and increases as the amount of swelling time increases. It has been reported earlier that the sol contains, except from the very small amount of unreacted chains, low molecular weight unreactive cyclic chains.[16]

C. Diffusion Measurements. Diffusion measurements were performed by using the pulsed-gradient spin-echo method[17] in the proton NMR at 33 MHz. The attenuation of the principal echo was measured at constant echo time $2\tau = 50$ ms as a function of the duration of each of a pair of applied magnetic field gradient pulses of magnitude G near 120 G/cm, separated by a time $\Delta = \tau = 25$ ms. A steady field gradient of magnitude $G_0 = 0.8$ G/cm was also applied at all times. This method of measuring self-diffusion (Brownian motion) of molecules, including the large-gradient non-FT variant of this method as applied to polymer systems, is extensively reviewed in the literature;[10] our own instrumentation,[18] experimental practices,[19] and data reduction models and software[20,21] were used as described with continuous refinements.[22]

Measurements were conducted at temperatures of 30.5, 80.5, and 110.5 °C, in that order. Later repeat measurements at 30 °C showed no effect of chemical degradation after exposure to the highest temperature for some 40 min, although some sample discoloration was observed. Measurements of spin–spin relaxation times T_2 were also performed, both to support the application of the polydispersity diffusion models[21] to be fitted to the data and to ensure that the spin echo from the network did not intrude significantly into the diffusion measurements. The transverse relaxation decays were subjected to a two-component decomposition,[23,24] which yielded relaxation times relatively insensitive to temperature and sample composition or treatment: a strong, rapidly decaying component [T_2(short) = 3–5 ms] attributed to the network, and a weak component with a modest distribution of relaxation times centered on T_2(long) = 18–27 ms, arising from the sol. The intensity of the sol component varied with sample treatment, becoming nearly unobservable for the fully extracted specimen.

Because the sol fractions were low, their diffusional spin-echo attenuations had correspondingly small signal-to-noise ratios, limiting the experimental precision. However, it was quite evident that the attenuations could not be interpreted in terms of a single diffusion rate, or even two discrete diffusion rates.[20] Instead, it was necessary in general to invoke a bimodal distribution of diffusivities consisting of a faster moving component and a broad distribution of components moving somewhat more slowly.[21,24] The data reduction and model fitting were performed off-line using the current version of our program DIFFUS5.[20–22] Because of the need to perform this composition, the precision of the determination of the component diffusivities was further degraded, to perhaps ±25%. The parameters being fitted to the echo attenuation data were the diffusivity of the fast-moving species, D(fast), the diffusion coefficient of molecules of number-average mass of the larger molecular species, $D(M_n)$, and f(fast), the fraction of the spin echo having $D = D$(fast). It is possible that the fast-diffusing species may be polydisperse as well, but the resulting diffusivity distribution is invariably obscured in the (initial) echo attenuation by its superposition on the slower component with its own distribution and so eludes analysis.

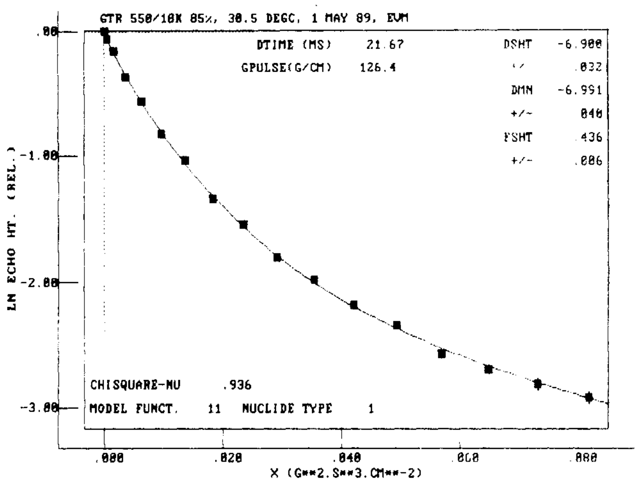

Figure 1. Diffusional attenuation of sol spin-echo at 50 ms as a function of gradient parameter $(\delta G)^2(\Delta - \delta/3)$. Measurement was made at 30.5 °C in the unextracted sample. Uncertainties are approximately the size of symbols; curved line denotes fitted two-component polydispersity model (see text).

III. Results and Discussion

A sample echo attenuation plot [logarithm of echo height vs $(\delta G)^2(\Delta - \delta/3)$] is shown in Figure 1. Upward concavity of such plots signals the presence of multiple diffusion rates, interpreted here in terms of the model discussed above.

The slower portion of the observed diffusivity spectrum requires further attention. The long PDMS chains used here had been characterized as having $M_n = 18\,000$, and their method of polymerization suggests that $M_w/M_n = 2$ is a reasonable estimate, the distribution resembling either the log-normal or the Schulz–Zimm forms. It was further assumed that the unreacted long chains in the sol have retained the form and width of the parent mass distribution. The likelihood that the mass averages would be higher than those of the parent distribution was accounted for in terms of an adjustable reference diffusivity. When these polydispersity parameters were provided to the modeling program, it was found that a Rouse-like proportionality of the diffusion coefficient D to M^{-1} was insufficient to reproduce the observed diffusivity distribution. It was therefore necessary to invoke entanglement between the larger sol molecules and the network (as well as among larger sol molecules); its onset was postulated for this polymer to occur near $M_c = 10\,000$,[25] above which D was to be proportional[21] to M^{-2}. This resulting model produced acceptable fits in all cases, indifferent to the choice of log-normal or Schulz–Zimm distribution, and represents a description of the polymer dynamics in keeping with current concepts.

The results of the analysis are collected in Tables II and III. Because of the substantial scatter of the numerical results, we prefer to display trends in terms of averages, either over extraction time (Table II) or over temperature (Table III), as appropriate. This aggregation is permissible here since sol fraction is temperature independent and the T_2 relaxation rates had very modest temperature dependences, while the diffusion rates had no discernible concentration dependence, seeing that the initial sol content was below 5%.

Table II describes the progress of the extraction of the sol. The specific spin-echo signal, proportional to the sol fraction in the absence of pronounced variation in spin–spin relaxation rates (see above), decreases asymptotically but nonexponentially, with a half-time initially <15 min but increasing later (see below). Significantly, while the

Table II
Spin-Echo Components in PDMS Sol[a]

extraction time	echo signal strength[b] (arb units)	f_{fast}[c]
0	142 ± 5	0.44 ± 0.05
15 min	51 ± 2	0.31 ± 0.04
30 min	34 ± 2	0.23 ± 0.04
60 min	14.7 ± 1	<0.06
90 min	14.1 ± 1	<0.07
5 days	<6[d]	

[a] Results represent averages over model interpretations of all available data taken at 30.5, 80.5, and 110.5 °C. [b] Echo height (sol) at 50 ms, per unit sample mass, and corrected to constant $1/T$ (K) before averaging. [c] Fraction of faster diffusing component of sol echo at 50 ms. [d] A trace of nonnetwork echo is observable but not measurable.

Table III
Component Diffusivities in PDMS Sols[a]

temp, °C	log [D(fast)][b]	log [$D(M_n)$][c]
30.5	−7.0 ± 0.1	−7.7 ± 0.1
80.5	−6.3 ± 0.1	−7.4 ± 0.1
110.5	−6.0 ± 0.1	−7.3 ± 0.1

[a] Results represent averages over model interpretations of all available data in samples extracted for 0, 15, 30, 60, and 90 min.[b] Diffusion coefficients expressed in cm^2 s^{-1}. [c] Model assumed M_n = 18 000, M_w = 36 000; entanglements retard diffusion of sol molecules above molecular mass 10 000.

NMR signal from the sol prior to extraction represents ca. 5% of the total signal (cf. Table I for the equivalent chemical result), small traces of echo signal not believed to arise from the network are still observable (although not measurable) after 5 days of extraction. This result suggests the degree of care necessary in providing an uncontaminated host network for further experiments, e.g., measuring the diffusion rate of new molecular species introduced into the network in trace quantities.

In a network assembled from a blend of short and long molecules, the sol would be expected to contain some of both types. The relative amounts may not closely reflect the proportions as originally supplied; because of differences in mobility, one might expect the smaller species to have greater success in reacting and thus be underrepresented in the initial sol. At first sight the opposite appears to be the case here. The smaller, hence faster moving, species constitutes 85 mol %, hence 15 wt % or less, of the preparation, but apparently some 44 wt % of the sol prior to extraction. The actual disproportion is likely to be less than evident here at 50 ms for two reasons. First, T_2 of the smaller species in the sol is probably somewhat longer than that of the larger species; this supposition was experimentally not directly confirmable (however, see below). Second, the faster diffusing component will also contain contributions from any unreacted curative as well as catalyst, which would also substantially exaggerate its relative magnitude. It should be pointed out that fractional proton NMR intensities are directly comparable to weight fractions only if the number of protons per weight unit is the same for the species compared; this is the case to a high approximation for short and long PDMS molecules, but not for PDMS vs curative or catalyst.

Extraction should be more efficient the smaller the molecules. It will be noted that the fraction of spin echo arising from the smaller species decreases as the extraction proceeds; no fast-moving component is, in fact, observable beyond 30 min of extraction. The data are not good enough to obtain separate extraction half-times for the two species but are semiquantitatively in agreement with a ratio of perhaps 3:1 in half-times.

This ratio is not likely to agree with the reciprocal ratio of sol diffusion rates of the two major species, because extraction takes place in the highly swelled state, having greater resemblance to a dilute solution with its lesser, hydrodynamic dependence of D on M. Table III in fact shows that the component diffusivities for the sol in the unswelled network differ by something like an order of magnitude, although the comparison is somewhat obscured by the polydispersity-related diffusivity distribution of the larger species and the higher apparent thermal activation energy of the smaller species.

The diffusion rate of the smaller species is within the anticipated range, but the motion of the number-average-mass members of the larger species seems to be somewhat faster than might be expected. Given the substantial polydispersity of the large species and the consequent large mass of the longest sol molecules, it is very likely that the T_2 of the latter resembles that of the network and is therefore too short to contribute to the spin echo at 50 ms. (This hypothesis would also help explain the difference between the weight fraction of short chains in the original blend and the surprisingly larger fraction of fast-moving molecules in the unextracted sol, discussed above.) While the model fitted to the data correctly accounts for this effect, the resulting fitted simulations and their numerical results were found to be quite sensitive to the detailed dependence of component T_2 and diffusivity on M within the polydisperse ensemble. Since these dependences were not precisely measurable here but depended to some extent on theoretical constructs or estimates, the absolute numerical values of $D(M_n)$ should be regarded with caution. However, the need to invoke entanglement/reptation effects for the largest sol molecules may be taken as firmly established.

IV. Concluding Remarks

We have studied the progress and efficiency of extraction of sol from model PDMS networks prepared by us from molecules of two species differing greatly in average length. The main analytic technique was the NMR-based pulsed-gradient method of measuring self-diffusion, supplemented by NMR relaxation; both were used to study molecular mobilities, mainly of the sol. Our findings may be summarized as follows:

(1) The reported work adds new knowledge on the subject of self-diffusion of polymers in melts.[26-28] It represents a novel use of bimodal model networks to elucidate their characterization by extraction techniques and to explore diffusivity behavior in general.

(2) The synthetic technique used (by us and others) results in a very low sol weight fraction less than 5%. This, however, leaves the networks essentially unusable as hosts for critical further studies unless sol extraction is performed.

(3) Extraction by swelling in toluene is successful provided it is sufficiently prolonged. For samples 1 mm thick, 90% or more of the lighter components of the sol is removed within the first hour, but many hours or several days are required to reduce the heaviest components to the same extent.

(4) In the unswelled network the diffusion rates of light and heavy PDMS molecules differ by at least an order of magnitude. The heaviest molecules appear to be entangled with the network since they diffuse much more slowly than the bulk of the polydisperse larger species.

(5) The combination of NMR relaxation and pulsed-gradient diffusion measurements is well suited for the study of sol in polymer networks. Diffusivity is more sensitive

to differences in the size of similar molecules than is spin-spin relaxation or chemical shift.

(6) It is conceivable that the methodology presented here could be used as a fractionation technique of laboratory-scale samples.

Model PDMS networks of this kind after sol extraction are eminently suitable as host materials in the study of molecular kinetics and dynamics in the presence of topological constraints. Work along these lines is in progress in our laboratories.

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Registry No. $Si(OEt)_4$, 78-10-4.

Cationic Transannular Polymerization of 1,5,9-Cyclododecatriene

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ABSTRACT: The cationic transannular polymerization of 1,5,9-cyclododecatriene initiated by $Al_2Et_3Cl_3$ or $AlEtCl_2$ is studied, and the effects of reaction conditions on the polymer yield are investigated. In accordance with the experimental infrared and nuclear magnetic resonance spectroscopic data, GC-MS analysis, and the solubility of the products, the resulting polymer is determined to be a linear oligomer consisting of tricyclic repeat units, of which the number-average molecular weight is ca. 1100-2200. The intramolecular cyclization of 1,5,9-cyclododecatriene reported earlier by Tolstikov et al. corroborated the conclusion given in this paper. The experimental results also indicate that *cis,trans,trans*-1,5,9-cyclododecatriene is much more prone to polymerize than *trans,trans,trans*-1,5,9-cyclododecatriene.

Introduction

The field of cationic transannular polymerization was opened by investigations concerning the polymerization of 2-methylene-5-norbornene[1] and 2,5-norbornadiene.[2] Typical examples of transannular polymerization are shown in Table I. However, no research work has been reported hitherto on the cationic transannular polymerization of 1,5,9-cyclododecatriene (CDT), although the ring-opening polymerization of CDT occurs in the presence of some chlorides of transition metals.[8,9]

In this work, the transannular polymerization of CDT initiated by $AlEtCl_2$ and $Al_2Et_3Cl_3$ was studied. The effects of reaction conditions, such as the kind of cationic initiator and coinitiator and the concentration of monomer, on the polymer yield were investigated. Combining the results of infrared and nuclear magnetic resonance spectroscopy and GC-MS analysis with the experimental data on isomerization of CDT reported by Tolstikov[10] and Antropimsova,[11] we concluded that the resultant polymer consists of tricyclic repeat units.

Experimental Section

Materials. 1,5,9-Cyclododecatriene was purified by shaking with concentrated sodium hydroxide solution three times at room temperature. It was then washed with dilute sulfuric acid and with water and predried with calcium chloride. The predried monomer was distilled at reduced pressure under an argon

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