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The Relaxation and Equilibrium Behaviour of Model Polyurethane Networks

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Summary

The mechanical, dielectric and rheo-optical behaviour of model networks prepared from OH-terminated poly(oxypropylene)triols and 4,4'-diphenylmethane diisocyanate with various molar ratios of hydroxyl to isocyanate groups, r_H = 0.95 to 1.7, was investigated. The observed independence of the stress-optical coefficient of r_H indicates the homogeneity of networks. Networks prepared with $r_H \approx 1$ exhibit a narrow transition zone indicating a narrow chain distribution. With increasing r_H, the transition becomes distinctly broader; dielectric measurements are well correlated with the mechanical ones. The equilibrium modulus markedly decreases with increasing r_H.

Introduction

Networks prepared from telechelic prepolymers by endlinking may serve as well-defined model systems, which may be employed in the investigation of relationships between structure and mechanical, dielectric and rheo-optical characteristics. Networks of this type were used in many cases, e.g., in the verification of molecular models of the equilibrium mechanical behaviour (REMPP et al. 1978, MARK 1979, OPPERMANN and REHAGE 1979, VALLES and MACOSKO 1979). In an ideal case, these networks may have a well-defined and virtually defectless structure. Especially networks of poly(oxypropylene)triols are homogeneous and possess a narrow chain length distribution (DUŠEK and ILAVSKÝ 1978, ILAVSKÝ et al. 1978). Calculation of the number of elastically active chains as a function of the initial composition using the theory of branching processes is comparatively simple for these systems in the ring-free case (DUŠEK et al. 1977). So far, the viscoelastic behaviour of homogeneous polyurethane networks has been studied in greater detail only by SHIBAYAMA and KODAMA (1966) for a comparatively complicated system toluylenediisocyanate-poly(oxypropylene)diol - poly(oxypropylene) triol - dipropylene glycol-water.

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This study reports an experimental investigation of the mechanical, dielectric and optical behaviour of networks obtained from poly(oxypropylene)triols and 4,4'-diphenylmethane diisocyanate with various molar ratios of hydroxyl and isocyanate groups.

Experimental

The networks were prepared from two poly(oxypropylene)triols (PPT) with various number average molecular masses (M=708 and 2630, determined by the GPC method) and 4,4'-diphenylmethane diisocyanate (MDI); the polymerization proceeded at 353 K for eight days between planeparallel Teflon plates, 10x10x0.1 cm^3 in size, with dibutyltin dilaurate as the catalyst. Samples were prepared with initial ratios of the concentrations of hydroxyl and isocyanate groups r_H = [OH]/[NCO] in the range 0.95-1.74 (Table I).

TABLE I

Mechanical, dielectric and optical characteristics of polyurethane networks

Sample	r_H	T_s^v K	T_s^d K	h^v	h^d	D_e MPa^{-1}	G_e MPa	$C_e.10^4$ MPa^{-1}	$-\delta.10^3$ K^{-1}
1	0.96	360	341	1.4	2.0	0.115	2.95	33.0	15.0
2	1.07	346	328	1.7	2.1	0.153	2.12	31.9	1.8
3	1.28	329	317	2.1	2.5	0.264	0.95	32.2	6.0
4	1.74	301	294	2.9	3.2	44.0	0.01	29.2	3.5
5	0.95	278	266	2.0	2.6	0.285	1.11	18.1	2.6
6	1.00	275	260	2.3	3.0	0.413	1.05	17.5	4.5
7	1.10	269	262	3.2	3.0	0.750	0.63	17.7	1.2
8	1.20	267	258	4.8	4.0	1.464	0.33	18.3	1.4

number average molecular mass M PPT: samples 1-4 M=708,
samples 5-8 M=2630

The OH group concentration in PPT was determined by the isocyanate method, viz., by a reaction of OH groups with phenyl isocyanate in excess followed by titration of unreacted phenyl isocyanate with dibutyl amine.

The linear viscoelastic creep behaviour was measured by using an apparatus described earlier (HAVRÁNEK 1965) in the time interval 10^{-2} - 10^3s and in the temperature range 220-350 K. The dielectric measurements were performed in the same temperature range at frequencies between 10^{-2} and 10^5 Hz. Using compliance curves D(t) recorded at temperatures T, a superimposed curve $D_p(t)$ was constructed at the reference temperature T_o according to the modified method of reduced variables (ILAVSKÝ et al. 1972) by plotting

$$D_p(t) = D(t)\,\frac{T}{T_o}\,(\rho_T/\rho_{T_o})^{1/3}\exp[\delta(T-T_o)] \qquad (1)$$

against t/a_T, where t is time, ρ is density, a_T is the shift factor and δ is a parameter characterizing the temperature dependence of unperturbed chain dimensions, determined from the temperature dependence of equilibrium compliance in the rubberlike region, D_e (Fig.1).

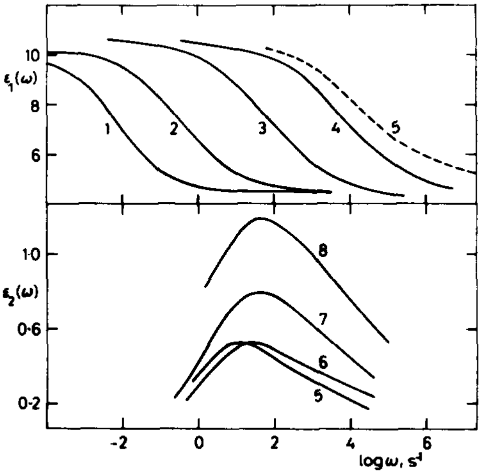

Fig.1
The time dependence of superimposed compliances $D_p(t)$ at the reference temperature T_o=340 K. The numbers at curves correspond to samples in Table I.

The $D_p(t)$ curves were used in the determination of the retardation spectra $L(\tau)$ (τ being the retardation time) of the individual networks by employing an approximation method of SCHWARZL and STAVERMAN (1952). The spectra widths h^v were determined from the dependence of $L(\tau)$ on log τ as values at the mid-height of the spectrum, L_m. Using the temperature dependences of the shift factor, characteristic temperatures of the Williams-Landel -Ferry equation T_S^W were determined (WILLIAMS et al. 1955).

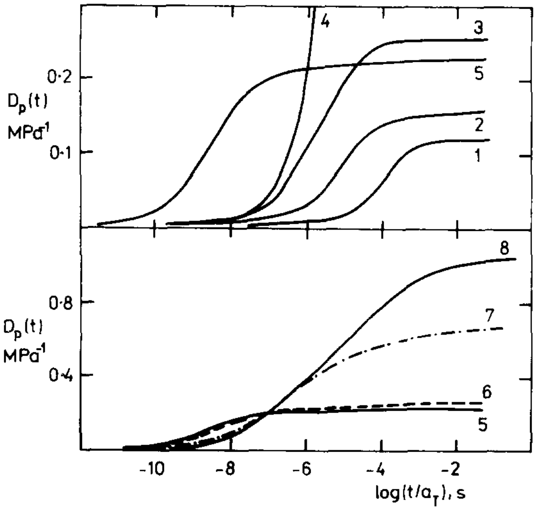

Fig.2
Dependences of the real part of complex permittivity $\varepsilon_1(\omega)$ on frequency ω for samples 1 to 5 (reference temperature T_o=300 k) and of the imaginary part of complex permittivity $\varepsilon_2(\omega)$ on ω for samples 5 to 8 (reference temperature T_o= =243 K)

Dielectric data (superscript d in Table I) were treated in a similar way; due to the wide frequency interval, the superposition method did not generally have to be used (Fig.2). From the phenomenological viewpoint, the course of the real part of permittivity $\varepsilon_1(\omega)$ in the first approximation is proportional to the course of compliance D(t), and the course of the imaginary part $\varepsilon_2(\omega)$ is proportional to the retardation spectrum $L(\tau)$, if we put $\omega = 1/t$ or $\omega = 1/\tau$ (McCRUM et al. 1967). A considerable asymmetry was observed in the high-frequency range of the ε_2 vs. log ω dependence; the widths of the dispersion range h^d were therefore assessed from the low-frequency part of ε_2 (Table I).

Rheo-optical measurements carried out at 340 K at relative extensions ($1 < \lambda < 1.1$) gave values of the equilibrium shear modulus G_e, deformational-optical function A_e and stress-optical coefficient C_e from

$$\sigma_e = G_e(\lambda^2 - \lambda^{-1}) \qquad (2)$$

$$\Delta n_e = A_e(\lambda^2 - \lambda^{-1}) \qquad (3)$$

and $C_e = \Delta n_e/\sigma_e$, where σ_e is stress related to the deformed cross-section and Δn_e is birefringence.

Results and Discussion

Main transition region. With the increasing molecular mass of PPT, the transition zone is considerably shifted towards shorter times or higher frequencies. Also the increasing r_H for samples with the molecular mass of PPT 708 displaces the dispersion region in the same way (cf.Figs 1 and 2). For samples with the molecular mass of PPT 2630 the displacement of the dispersion region on the time or frequency axis is indistinct. The temperature position of the main transition region characterized by T_s is shifted to lower temperatures both with increasing r_H and M, the shift with r_H again being more pronounced for samples with M=708 (cf.Table I). The somewhat higher T_s^v values compared with T_s^d ($T_s^v \approx T_s^d + 10$ K) indicate differences in the detailed process of releasing chain motion in the mechanical and dielectric experiment, and are quite usual (McCRUM et al. 1967). The displacement of the transition region to shorter times, or the decrease in T_s both with r_H and M, may be assigned to the decrease in the MDI content, i.e. to the decrease in the concentration of polar urethane groups. This is demonstrated by the practically universal dependence of T_s vs. MDI content, irrespective of r_H and M. The decrease in the concentration of elastically active network chains (EANC) with increasing r_H and M is reflected in this shift probably only to a minor extent.

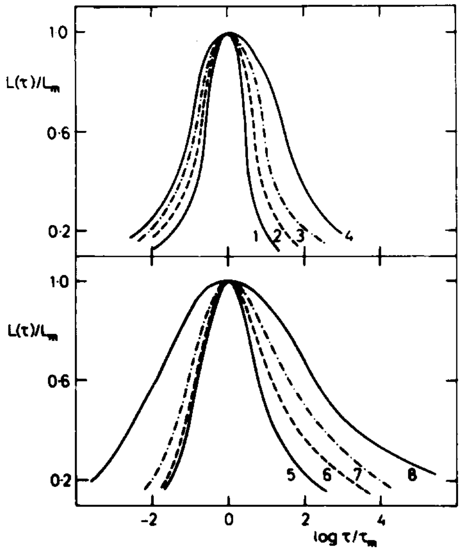

Fig.3
Reduced retardation spectra $L(\tau)/L_m$ of samples 1 to 8. τ_m is the retardation time corresponding to the maximum L_m of the spectrum $L(\tau)$

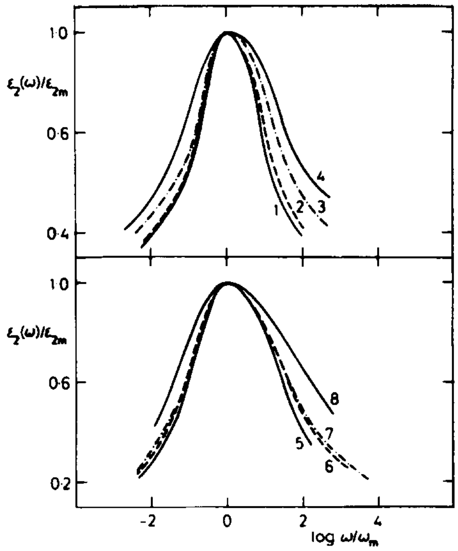

Fig.4
Reduced dependence of $\varepsilon_2(\omega)/\varepsilon_{2m}$ of samples 1 to 8. ω_m is a frequency corresponding to the maximum ε_{2m} of the imaginary part of permittivity $\varepsilon_2(\omega)$

Networks prepared from PPT with M=708 and $r_H \approx 1$ exhibit a very narrow transition region (measured mechanically and dielectrically, Figs 3 and 4, Table I), in agreement with their model character, especially with the small length of EANC and their narrow distribution. Both the increasing r_H (at constant M PPT) and the molecular mass of PPT cause an increase in the width of the transition zone (Figs 3 and 4), in agreement with the increasing length of EANC and a broader chain length distribution in the network. The observed pronounced broadening of dispersion dielectric regions at high frequencies is probably due to the contribution of a secondary transition; this effect increases with increasing M of PPT and r_H (reaching ≈ 1.5 log decade for sample 8). It is of interest that, with the exception of sample 4, the dependence of h^v and h^d vs. the equilibrium modulus G_e is universal.

Rubberlike region. The product D_eT was found to be markedly temperature-dependent (D_e was determined from viscoelastic measurements) in the rubberlike region.

This dependence was used in the determination of the parameter δ (Table I). δ thus determined is subjected to a comparatively great error (it varies between $-1.2\mathrm{x}10^{-3}$ and $-6\mathrm{x}10^{-3}\mathrm{K}^{-1}$), and the average δ value (without considering sample 1) is $-3\mathrm{x}10^{-3}\mathrm{K}^{-1}$. The average δ is higher by an order of magnitude than the one determined earlier for a polyurethane network consisting of poly(oxypropylene)diol, MDI and trimethylolpropane (CONWAY 1960, TANAKA and YOKOYAMA 1968, ILAVSKÝ and DUŠEK 1976), which may be a consequence of the of the higher content of polar urethane groups in PPT networks, but also of a not fully achieved equilibrium in the determination of D_e. In agreement with the high δ values determined from viscoelastic measurements, the low-frequency value of ε_1 of these samples decreases with increasing temperature.

The stress-optical coefficient C_e is independent of r_H for both series of networks (Table I), thus bearing evidence of the homogeneity of systems under study, in agreement with the theory of Gaussian networks (TRELOAR 1958). The lower C_e observed for networks with a higher M PPT is caused by the lower concentration of urethane groups in EANC. The equilibrium compliance values D_e determined from viscoelastic measurements correlate well with the equilibrium modulus G_e(G_e=1/3D_e) at the same temperature of measurement (Table I). With increasing r_H and molecular mass M PPT the modulus G_e decreases (D_e increases) as expected as a result of the lower EANC concentration in the networks.

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