periments, but if a point at 30.2 °C is not taken into account, the seven most concentrated solutions, quite certainly lying in the semidilute concentration range, have been centrifuged at a nearly constant temperature (24.5–25.1 °C). These solutions yield a good straight line of slope −0.64. The conclusion which may be drawn from these results and our own results is that in the semidilute concentration range the sedimentation coefficient s obeys a $c^{-\alpha}$ power law, where the exponent α takes a spectrum of values with presently ill-defined limiting values, but which extends for polymers dissolved in good solvents at least in between 0.64 and 0.82.

Acknowledgment. The authors thank Professors W. H. Stockmayer and G. Weill for useful discussions and Mr. J. F. Gueguen for fractionating the polystyrene samples.

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Viscoelastic Properties of a Dilute Polymer Solution at Elevated Pressures and Comparison with Molecular Models

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Received July 21, 1978

ABSTRACT: Measurements at 98.9 °C (210 °F) and pressures to 172 MPa (25 000 psi) with an oscillating quartz crystal apparatus show that the shear storage modulus and dynamic viscosity of a 4 wt % solution of poly(alkyl methacrylate) in a base oil can be predicted at high pressures by using appropriate values of pressure-dependent parameters in the Zimm model for dilute polymer solutions. Measurements on the base oil gave no evidence of viscoelastic behavior at 98.9 °C (210 °F) and pressures to 276 MPa (40 000 psi).

There have been few measurements of the viscoelastic properties of dilute polymer solutions at elevated pressures and there has been little discussion of the applicability of molecular models, such as those by Rouse[2] and Zimm,[3] to calculation of viscoelastic properties at elevated pressures. Measurements that have been made at elevated pressures have included solutions of polyisobutylene,[4] polymethacrylates,[4] and poly(alkyl methacrylate)[5] in base oils at pressures to 104 MPa (15 000 psi). These measurements indicate viscoelastic behavior over the entire pressure range. However, the relative contribution of elasticity to the overall behavior decreased with pressure.[5] It was also suggested that the hydrodynamic interaction between the polymer and the solvent did not change over this pressure range,[4] so no change in interaction would have to be considered in applying molecular models to this pressure range. However, none of the reported data were compared with predictions of molecular models. This paper reports data obtained at pressures to 172 MPa (25 000 psi) for a 4 wt % solution of poly(alkyl methacrylate) and compares the data with the predictions of the Rouse and Zimm models.

The Rouse and Zimm models describe the frequency-dependent behavior of the shear storage modulus, $G'(\omega)$, and the dynamic viscosity, $\eta'(\omega)$, of dilute solutions of polymers with a single molecular weight in a Θ solvent (a poor solvent which causes negligible expansion of the polymer by solvent action). The models differ in the way they treat the frictional interaction between the polymer and solvent. In the Rouse, or free-draining, model the viscous resistance of a hypothetical subdivision of the polymer is unaffected by the presence of other subdivisions. In the Zimm, or nondraining, model viscous resistance is dominated by the presence of the other sub-

0024-9297/79/2212-0296$01.00/0

Table I
Characterization of Fluids Studied

property	this study	ref 9 and 10
Base Oil[12]		
density, g/cm^3 at 20 °C (68 °F)	0.8591	0.8602
viscosity, cSt at 37.8 °C (100 °F)	31.0	33.7
viscosity, cSt at 98.9 °C (210 °F)	5.13	5.40
molecular weight	395	404
Poly(alkyl methacrylate)[13]		
number-average molecular weight	6.05×10^4	
weight-average molecular weight	9.65×10^5	
viscosity-average molecular weight	5.6×10^5	5.6×10^5
% viscosity loss due to polymer following treatment as per ASTM D-2603 in standard base oil B	34.7	33.8
molecular weight of average monomer	213	

divisions. The frequency dependence of the shear storage modulus and the dynamic viscosity are described by:

$$G'(\omega) = (cRT/M)\sum_{1}^{N}(\omega\tau_k)^2/(1 + (\omega\tau_k)^2) \qquad (1)$$

$$\eta'(\omega) = \eta_s + (cRT/M)\sum_{1}^{N}\tau_k/(1 + (\omega\tau_k)^2) \qquad (2)$$

where η_s is the solvent viscosity at the limit of zero shear rate, T is the absolute temperature, c is the polymer concentration as weight per volume of solution, ω is the angular frequency, R is the gas constant, and N is the number of submolecules into which the polymer is divided. The relaxation times, τ_k, for different modes of motion of the polymer chain are for the Zimm model

$$\tau_k = 1.71(\eta - \eta_s)M/\lambda_k'cRT \qquad (3)$$

and for the Rouse model

$$\tau_k = 6(\eta - \eta_s)M/\pi^2k^2cRT \qquad (4)$$

η is the solution viscosity at the limit of zero shear rate.

The first values of the numerical coefficients λ_k' in eq 3 are: 4.04, 12.8, 24.2, 37.9, 53.5, 70.7, and 89.4.[6] Subsequent values of λ_k' can be approximated by[6]

$$\lambda_k' = (\pi^2k^{3/2}/2)(1 - 1/2\pi k) \qquad (5)$$

The models represented by the above equations can only be applied[7] if the series in eq 1 and 2 converge for $k < N$. N is approximately $M/20M_0$, where M_0 is the molecular weight of a monomer,[8] so the models are only applicable if the series in eq 1 and 2 converge for

$$k < M/20M_0 \qquad (6)$$

This paper considers direct extension of eq 1 through 4 to high pressures by using the appropriate values for the pressure-dependent parameters density, ρ (required to account for changes in C with pressure), η, and η_s in eq 1 through 4.

Experimental Section

Materials. A paraffinic base oil and a 4 wt % solution of poly(alkyl methacrylate) (a copolymer averaging nine carbon atoms in the ester grouping) in the base oil were studied. This particular system was studied because the base oil and solution are very similar to fluids investigated previously,[9,10] so available data could be utilized in analyzing the results from this study.[11] Values of the parameters characterizing the fluids used in this study and the corresponding fluids from ref 9 and 10 are listed in Table I. It is evident from Table I that the base oil and polymer used in this study are similar to those used in the previous study.

Table II
Estimated Uncertainties in Measured Values for 20-kHz-Quartz-Crystal Viscometer

viscosity range, P	uncertainty in viscosity measurements, %	uncertainty in shear storage modulus measurements, %
0.0–0.02	±15	±15
0.02–1	±10	±25
1–5	±15	±50

This system was also studied because it is representative of a viscosity-index improver in a base oil and thus can give information about the behavior of multigrade lubricating oils. In practice precipitation of the viscosity-index improver from the base oil cannot be allowed, so it is reasonable to qualitatively characterize this system as a solution of a polymer in a good solvent.

Equipment. An oscillating quartz crystal apparatus[4,5,14,15] with a fundamental frequency of 20 kHz in air at atmospheric pressure was used to measure the viscoelastic properties. This type of viscometer is particularly well-suited to high-pressure measurements not only because high-pressure sealing problems are minimized, but also because viscous heating of the test fluid is negligible even at high frequencies.

With this kind of viscometer, properties of the test fluid are related by the following equations to electrical measurements of the resonant frequency, f, and resistance at resonance, R_E, of the crystal immersed in the fluid.

$$\eta' = G''/\omega = 2X_MR_M/\omega\rho \qquad (7)$$

$$\eta'' = G'/\omega = (R_M^2 - X_M^2)/\omega\rho \qquad (8)$$

$$X_M = (f_0 - f)/K_f \qquad (9)$$

$$R_M = (R_E - R_{E_0})/K_r \qquad (10)$$

ρ is the fluid density and the parameters f_0, K_f, R_{E_0}, and K_r are related to properties of the crystal. They were determined by calibration in Newtonian fluids for which the viscosity and density were known functions of pressure and temperature. Details of the calibration are given elsewhere.[16]

Because the sensitivity and stability of the measuring equipment changes with fluid viscosity, the accuracy of measurements with this type of viscometer has been found to vary with the viscosity of the fluid being measured. Estimated uncertainties for various viscosity ranges are summarized in Table II. As indicated in Table II, the uncertainty of the shear storage modulus is considerably greater than the uncertainty of the viscosity. The reason is that the calculation of the shear storage modulus by eq 8 involves the difference of squares of numbers of similar magnitudes while no such difference is involved in the viscosity calculation by eq 7. Reduced equipment sensitivity at viscosities greater than 5 P precludes obtaining meaningful data for viscosities greater than 5 P.

Pressure was measured by using a Carey–Foster bridge to measure the resistance of a coil of manganin wire which was in the high-pressure environment. It is estimated that pressures were measured to an accuracy of better than ±0.5% for pressures of 68.9 MPa (10 000 psi) or greater.

The pressure cell was heated by four electric heaters in contact with the cell. Temperature control was maintained to better than ±0.3 °C (±0.5 °F).

Results and Discussion

Base Oil. Figure 1 shows viscosity-pressure data obtained with the oscillating crystal apparatus for the paraffinic base oil at 98.9 °C (210 °F) and a measurement frequency of 1.26×10^5 rad/s. Viscosities were calculated from the electrical measurements according to eq 7, 9, and 10 with density-pressure data obtained from ref 9. Viscosities obtained at a shear rate of 10^4 s^{-1} with capillary viscometers[9] are also shown in Figure 1.

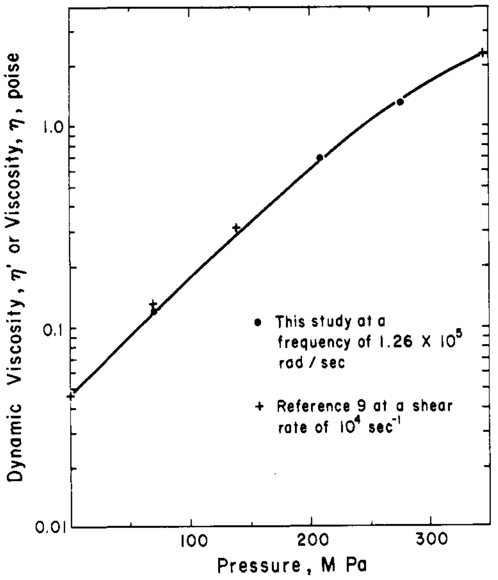

Figure 1. Effect of pressure on the viscosity at 98.9 °C (210 °F) of a paraffinic base oil.

No elastic behavior of the base oil was observed with the crystal apparatus (values of G' significantly greater than zero were not measured), so the viscosity of the base oil will be independent of frequency for frequencies up to 1.26 $\times 10^5$ rad/s at 98.9 °C (210 °F) over this pressure range. Measurements with capillary viscometers[9] indicate Newtonian behavior for shear rates nearly the same as the frequency used with the crystal apparatus[17] and for the same pressure range and temperature. Since measurements at a frequency ω are qualitatively equivalent to measurements at a shear rate $\dot{\gamma} = \omega$, the oscillating crystal and capillary measurements show that there is no frequency or shear rate effect on the viscosity for these conditions. Thus the excellent agreement between the two sets of data in Figure 1 is not a result of frequency or shear rate effects compensating for measurement differences but rather shows that measurements by the two techniques corroborate each other.

Polymer Solution. Dilute-Solution Requirement. Data for the polymer solution and predictions of the molecular models are most easily compared if the solution is dilute enough to satisfy the dilute-solution requirement of the models. The basis for determining the concentration limit set by this requirement was the observation[7] that there should be only moderate interpenetration of the peripheries of the polymer coils if the product of concentration c and the intrinsic viscosity $[\eta]$ is less than 2. Thus the dilute-solution requirement used was

$$c[\eta] < 2 \tag{11}$$

The intrinsic viscosity is given by either

$$[\eta] = \lim_{c \to 0} (\eta - \eta_s)/\eta_s c \tag{12}$$

or

$$[\eta] = \lim_{c \to 0} [(\ln \eta/\eta_s)/c] \tag{13}$$

Application of eq 11 to the conditions of this study requires knowledge of the intrinsic viscosity of the solution at atmospheric pressure and at elevated pressures. Rough estimates of intrinsic viscosities at atmospheric pressure, 69 and 138 MPa (10 000 and 20 000 psi), were obtained by the following procedure.

The zero shear rate viscosity of a 4 wt % solution of the polymer was estimated at each pressure by visual extrapolation to zero shear rate of viscosity-shear rate data in ref 9. The same was done for an 8 wt % solution for the same pressures. The viscosity of the base oil, η_s, and solution densities (which were independent of polymer concentration) were also obtained from ref 9 for the same pressures. These viscosities and densities are listed in Table III. They were used to calculate values of $(\eta - \eta_s)/\eta_s c$ and $(\ln \eta/\eta_s)/c$ for each pressure. Linear extrapolations of $(\eta - \eta_s)/\eta_s c$ and $(\ln \eta/\eta_s)/c$ to zero concentration gave estimates of the intrinsic viscosity at each pressure. Linear extrapolations were necessary because data were only available for two concentrations. Intrinsic viscosities and the products $[\eta]c$ obtained from both sets of data are listed in Table III.

Table III
Parameters Related to a Dilute-Solution Requirement of a 4 wt % Solution of Poly(alkyl methacrylate) at 98.9 °C (210 °F) and Elevated Pressures

parameter	atmospheric pressure	69 MPa	138 MPa
solution density,[a] ρ, g/cm^3	0.809	0.849	0.876
base oil viscosity,[a] η_s, P	0.046	0.12	0.30
viscosity of a 4 wt % solution,[a] η, P	0.12	0.31	0.76
viscosity of an 8 wt % solution,[a] η, P	0.24	0.65	1.6
From $(\eta - \eta_s)/\eta_s c$ Correlation			
$[\eta]$, cm^3/g	34	28	26
$[\eta]c$	1.1	0.95	0.90
From $(\ln \eta/\eta_s)/c$ Correlation			
$[\eta]$, cm^3/g	34	30	29
$[\eta]c$	1.1	1.0	1.0

[a] Obtained from data in ref 9.

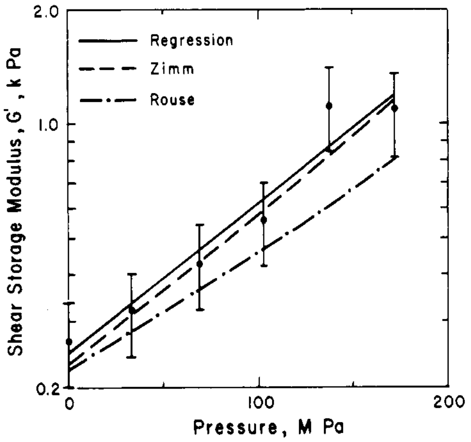

Figure 2. Effect of pressure on the shear storage modulus of a 4 wt % solution of poly(alkyl methacrylate) in a paraffinic base oil at 98.9 °C (210 °F) and 1.26 × 10^5 rad/s and comparison with predictions of the Zimm and Rouse models.

Because of possible errors in extrapolating the viscosity-shear rate data to zero shear rate and in approximating $(\eta - \eta_s)/\eta_s c$ vs. c and $(\ln \eta/\eta_s)/c$ vs. c relations by straight lines, the intrinsic viscosities and the products $[\eta]c$ in Table III are only approximate. However, eq 11 is so easily satisfied by the results of either correlation that there is little doubt that the solution used was dilute enough to allow comparison with the models.

Shear Storage Modulus and Dynamic Viscosity. Data in Figure 2 show the effect of pressure on the shear storage modulus, G', and data in Figure 3 show the effect of pressure on the dynamic viscosity, η'. These data are also tabulated in Table IV. The solid lines in Figures 2 and 3 are least-squares lines for linear relations between

Table IV
Properties of a Base Oil and a 4 wt % Solution of Poly(alkyl methacrylate) in the Base Oil at 98.9 °C (210 °F) and Elevated Pressures

	pressure, MPa					
property	atm	34.4	68.9	103	138	172
solution viscosity,[a] η, P	0.12	0.19	0.31	0.48	0.76	1.1
base oil viscosity,[a] η_s, P	0.046	0.077	0.12	0.19	0.30	0.44
solution or base oil density,[a] ρ, g/cm^3	0.809	0.829	0.849	0.864	0.876	0.891
shear storage modulus of solution, G', kPa	0.27	0.32	0.43	0.56	1.1	1.1
dynamic viscosity of solution, η', P	0.086	0.13	0.22	0.29	0.40	0.59

[a] Obtained from data in ref 9.

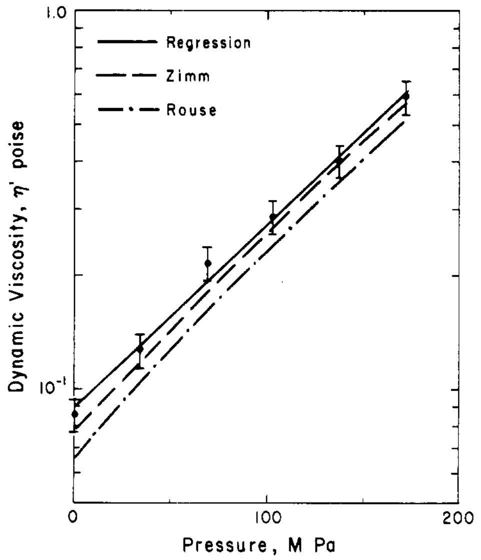

Figure 3. Effect of pressure on the dynamic viscosity of a 4 wt % solution of poly(alkyl methacrylate) in a paraffinic base oil at 98.9 °C (210 °F) and 1.26 × 10^5 rad/s and comparison with predictions of the Zimm and Rouse models.

the log of the shear storage modulus (Figure 2) or the log of the dynamic viscosity (Figure 3) and pressure. The correlation coefficient for the shear-storage modulus data is 0.97 and for the dynamic viscosity data it is 0.99. Error brackets in these figures indicate the estimated range of uncertainty for the data points. The data are for 98.9 °C (210 °F) and a measurement frequency of 1.26 × 10^5 rad/s.

Predictions obtained by using the appropriate values of the pressure-dependent parameters, η, η_s, and ρ, in the Zimm and Rouse models are shown by the interrupted lines in Figures 2 and 3. Values for these parameters are listed in Table IV and were obtained directly from, and by interpolation of, data in ref 9. The predictions are based on the weight-average molecular weight.

An upper limit of 150 was used for the summations in eq 1 and 2. Calculations showed that the series do converge for a limit of 150. Data in Table I show that $M/20M_0 = 226$ for this polymer, so use of 150 as the upper summation limit also satisfies the restriction given in eq 6.

Although the predictions of the Zimm model agree with the regression line describing the shear-storage-modulus data (Figure 2) better than the predictions of the Rouse model, the predictions of both models agree, within the limits of uncertainty of the measurements, with these data. Therefore, it is possible to describe these data by either model and it is not possible to distinguish between the applicability of the models on the basis of these data.

The predictions of the Zimm model agree with the dynamic viscosity data (Figure 3), but the predictions of the Rouse model are not within the limits of uncertainty of the data. Therefore, the Zimm model is more suitable for describing these dynamic viscosity-pressure data.

Thus, information in Figures 2 and 3 shows that at this temperature and frequency the measured viscoelastic properties of this solution at elevated pressures can be described by using high-pressure values of pressure-dependent parameters in the Zimm model.

The Zimm and Rouse models strictly apply only to Θ conditions (at which there is negligible expansion of the polymer by solvent action). Since this solution is not near Θ conditions agreement between the predictions of the Zimm model and the data suggests that solvent action has only a minor effect under the conditions of these measurements.

Furthermore, the agreement obtained by using the weight-average molecular weight in the models suggests that the effect of the broad molecular weight distribution is adequately accounted for by using the weight-average molecular weight for the combinations of pressure, frequency, and temperature investigated. Data for dilute polystyrene solutions at atmospheric pressure[18] suggest that use of the weight-average molecular weight will also be adequate at higher frequencies, but will be less adequate at lower frequencies.

Conclusions

Data showing the effect of pressure on the shear storage modulus and dynamic viscosity of a 4 wt % solution of poly(alkyl methacrylate) in a base oil can be described by using appropriate values of pressure-dependent parameters in the Zimm model for dilute polymer solutions. The measurements were made at 98.9 °C (210 °F) and pressures to 172 MPa (25 000 psi) with an oscillating quartz crystal apparatus.

Similar measurements on the base oil gave no evidence of viscoelastic behavior at 98.9 °C (210 °F) and pressures to 276 MPa (40 000 psi).

Acknowledgment. The author is grateful to: the Sun Oil Co. for supplying the base oil and the data for characterizing it, the Rohm and Haas Co. for supplying the polymer and data for characterizing it, Tom T. Charng for assisting with the experimental work, and C. M. Sliepcevich and Walter J. Ewbank for assistance throughout the investigation. This investigation was supported by NSF Grant GK-3651.

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Viscoelastic Properties of Poly(pivalolactone)

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Received November 13, 1978

ABSTRACT: The viscoelastic properties of poly(pivalolactone) (PPL) have been investigated in the linear range using stress–relaxation and dynamic-mechanical measurements. Under the conditions that the sample was isotropic and insensitive to relative humidity, Ferry's reduction method was applied without using translations along the vertical axis. A horizontal shift factor was determined at each temperature, which satisfactorily agreed with the WLF equation in the transition region. The apparent activation energy of PPL was temperature dependent and passed through a maximum near T_g whose value was found to be 369 ± 3 K. The relaxation spectrum was calculated according to the first method of approximation of Schwarzl and Staverman, and it was found to be flat with a complicated fine structure. Two absorption peaks were determined. The low-temperature γ peak, around 300 K, was ascribed to a relaxation process in the crystalline phase of the polymer while the high-temperature β peak was related to the glass-transition process.

Among polylactones based on the skeletal formula $(\text{-CH}_2\text{CR}_1\text{R}_2\text{COO-})_n$, poly(pivalolactone) (PPL) has been the most extensively studied because of its technological importance.[1-3] The practical and technological interests appeared since the polymer has been commercially spun to give fibers.[1,2] Moreover PPL has been found to have reinforcing properties when prepared in copolymers of the general structure ABA where A represents a PPL block and B an elastomer, for example, poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL). The mechanical properties of PPL/PMPPL ABA copolymers were reported similar to those of commercial styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS) copolymers.[4]

More recently, it was shown that grafting of short (M_n ~ 500–4000) chains of PPL onto various elastomeric backbone polymers, including ethylene–propylene–diene, alternating ethylene–ethyl acrylate copolymer, and poly(ethyl acrylate), produced a new type of thermoplastic elastomer with outstanding physical properties, such as solvent resistance resilience, abrasion resistance, and heat and aging stability.[5-9] ABA triblock copolymers containing 35–45% PPL made from polyisoprenes (M_n ~ 40000) could be melt-spun into fibers showing excellent mechanical properties.[10] In each case, the outstanding properties of these PPL-graft elastomers were related to the hard segments of PPL which act as cross-linking sites and reinforcing filler particles.

In view of the commercial importance of PPL, its thermal and crystalline properties have been investigated.[11-19] But surprisingly, its mechanical properties have not been studied despite the importance of this investigation in order to know the performance of PPL as a commercial film or fiber.

It is then the purpose of the present paper to investigate the viscoelastic behavior of PPL. On one hand, these measurements will lead to the determination of the glass transition temperature of PPL using stress–relaxation as well as dynamic methods. On the other hand, PPL is a highly crystalline material and little is known about the viscoelasticity of highly crystalline polymers. The results obtained in this study, along with investigations made on other crystalline polymers, may serve as a basis in checking up theoretical ideas in that area.

Experimental Section

The PPL sample (No. 100–36) used in this study was supplied by the Shell Laboratories in Amsterdam. Its viscosity average molecular weight, determined in a trifluoroacetic acid solution at 293 K, was 280000 $\text{g}\cdot\text{mol}^{-1}$.[19] The polymer contained a small amount of stabilizer.

The polymer films were obtained from a laboratory press. The samples were melted at 523 K for 10 min and they were rapidly quenched in water at room temperature, annealed at 468 K for 6 h, and then used. Under these conditions, PPL is a highly crystalline material and it is uniquely found by X-ray diffraction in the α form which is characterized by a 2_1 helical conformation of the chains.[11-13] DSC measurements, using indium as calibration standard, gave an enthalpy of fusion of 118 $\text{J}\cdot\text{g}^{-1}$ which corresponds to 80% crystallinity. The specimen is very brittle reaching an ultimate elongation lower than 10% even above 440 K.

Relaxation measurements were carried out at different temperatures on an Instron tester (table Model 1130) which we used as a relaxometer. Before each measurement, the sample specimen was preconditioned at zero strain in the jaws of the relaxometer, at least 1 h at the desired temperature. All series of measurements were performed starting from the highest measuring temperature. It was found that under these conditions, the relaxation curves were reproducible. This result indicates that there is no change in the structure of the sample due to heat treatment. Moreover, the sample was found to be insensitive to relative humidity. For relaxation measurements, samples having a thickness of 90 μm were used. For dynamic mechanical measurements, thicknesses of the order of 60 μm were necessary.

In order to ascertain that the measurements were restricted in the linear range of viscoelasticity, two different tests were undertaken at 351 K. According to the hysteresis loop method,[20]

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