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A Segmented Polyurethane Elastomer with Liquid Crystalline Hard Segments. 2. Rheological Study

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Received March 22, 1994; Revised Manuscript Received October 24, 1994[⊛]

ABSTRACT: The linear viscolastic properties of a segmented polyurethane referred to as LCPUE-1000 have been studied. LCPUE-1000 is a microphase-separated polymer with submicron mesophases as physical cross-links, and its rheological study indicates a broad transition from a viscoelastic solid to a viscoelastic liquid at the isotropization temperature of the mesophase. Furthermore, it has been found that time–temperature superposition applies in the isotropic state (160 to 110 °C). We conclude that the aggregation of liquid crystalline hard segments does enhance the connectivity of the molecular structure, and this is supported by the results of a kinetic study with dynamic mechanical spectroscopy (DMS). Physical gelation studies identify a liquid/solid transition when cooled to 106 °C or below and show the characteristic critical behavior at the gel point with a power law relaxation spectrum at low frequencies. Estimates are given for the relaxation exponent and the stiffness of the critical gel.

Introduction

Segmented polyurethane elastomers are an important class of polymeric materials consisting of thermodynamically incompatible hard and soft segments. The existence of microphase-separated domains, caused by aggregation of the hard and soft segments, has been well established. In order to achieve an anisotropic mesophase[1] in the hard domains, the mesogenic units are introduced as chain extenders.

The rheological behavior of thermotropic liquid crystalline polymers (TLCP) has been studied[2–6] for their unconventional phenomena which depend upon temperature and phase morphology. The viscosity of the nematic phase, for example, is usually considerably smaller than that of the isotropic phase, except at low frequencies or shear rates, where the viscosity grows to very large values which might be explained as a yield stress.

For the present study, the chemical structure of a main-chain TLCP is interrupted by soft segments. This alternating chain structure results in a two-phase morphology comprised of mesophasic hard and amorphous soft domains. A preceding paper[1] describes the synthesis and physical characterization of the material referred to as LCPUE-1000. A DSC experiment with a heating rate of 1.5 K/min shows the glass transition temperature of the soft segment at −51 °C and the isotropization of the mesophase occurring over a wide range from 110 to 144 °C. The breadth of the transition originates from the mesophase size distribution and from diffuse interfaces between the mesophasic and the amorphous domains. Here, we use rheological means to probe this thermal process and to further understand the viscoelastic solid/liquid transition.

Gelation or gel formation is a connectivity transition which results in a change of viscoelastic properties. On the molecular scale, this process is caused by cross-linking from either chemical covalent bonds or physical interactions. On the macroscopic scale, the gelation results in a liquid/solid transition, which can be monitored by means of rheology. Here, it should be pointed out that the term "solid" means the rubberlike state of a cross-linked polymeric material. It is not intended to suggest a glassy or even crystalline body with a clearly defined melting temperature.

In physically cross-linking processes, hard segments of macromolecules can aggregate to form physical junctions via hydrogen bonds, van der Waals forces, electrostatic attractions, and others. If the lifetime of the junctions is sufficiently long and molecular clusters grow in size, the polymer will exhibit a liquid/solid transition with a critical behavior at the transition point. The zero-shear viscosity diverges to infinity, and an equilibrium modulus starts to grow from zero after the gel point. Near the gel point, small-amplitude oscillatory shear is the preferred method in rheological experiments since it probes the sample without rupturing the evolving structure. Dynamic mechanical spectroscopy (DMS) is used within the linear viscoelastic range to obtain complex moduli[7]

$$G^* = G' + iG'' \qquad (1)$$

where G' represents the in-phase or elastic component and G'' the out-of-phase or dissipative component of G^*.

Chambon and Winter[8,9] have pointed out that, at the critical gel point of a polymer, the frequency dependence of the dynamic moduli follows a power law:

$$G_c' = G_c''/\tan \delta_c = S\omega^n\Gamma(1-n) \cos \delta_c$$
$$\text{for } 0 < \omega < \omega_0 \quad (2)$$

where $\Gamma(1-n)$ is the gamma function, S the gel stiffness, ω the frequency, and n the relaxation exponent. The subscript c indicates the validity of the equation at the critical gel point. Furthermore, the loss angle becomes frequency independent at this transition point, and n can be calculated according to:

$$\delta_c = n\pi/2 \quad \text{with } \tan \delta_c = (G''/G')_c \quad (3)$$

Winter and co-workers have used DMS to study physical gelation.[10,11,19] For example, the gelation of a TPE–polypropylene comprised of multiple blocks of stereo-
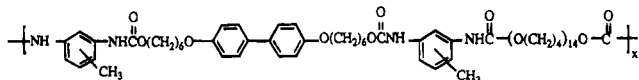
Figure 1. Chemical structure of LCPUE-1000.

regular and stereoirregular sequences is driven by the crystallization of the stereoregular block; the relaxation modulus at the physical gel point obeys the power law (eq 2). The validity of this equation is attributed to the critical gel's structural self-similarity.

Experimental Section

Materials.[1] The polymer used in this study was synthesized via solution polymerization. In the first stage of the reaction, a prepolymer was prepared from poly(tetramethylene oxide) (M_w = 1000) and the 1:1 mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate at 100 °C. This was followed by the chain extension of the mesogen 4,4'-bis[(6-hydroxyhexyl)oxy]biphenyl. The resulting polymer, referred to as LCPUE-1000 (Figure 1), has 42.3 wt % of hard segments. The average molar mass (M_w) determined by gel permeation chromatography in a THF solvent was found to be 75 400 (relative to polystyrene standards) with a polydispersity index of about 2.

Sample Preparation. Samples for rheological measurements were molded at 150 °C under vacuum and then slowly cooled down to room temprature at a rate of 5 K/min.

Rheological Measurements. Small-amplitude oscillatory shear experiments were performed on a Rheometrics dynamic spectrometer (RDS) 7700 using concentric disk fixtures, with a disk diameter of 25 mm and a gap width of about 1 mm after thermal adjustments, which assumed a fixture expansion of 1 μm/K. A nitrogen atmosphere was used to prevent oxidation in the experiments above 80 °C.

In order to investigate the material in its linear viscoelastic region, the periodic shear strain was varied from 0.05 to 0.25 in the higher temperature range (100–160 °C) and from 0.0125 to 0.02 in the lower temperature range (0–100 °C). Dynamic shear frequencies ranged from 0.1 to 500 rad/s. The viscoelastic properties of the sample were obtained from the oscillatory strain and its periodical torque response.

The isothermal consecutive frequency sweep (CFS) method allowed us to track the kinetics of the physical gelation process. The measurements were made with a strain of 0.02 in the frequency range of 0.1–10 rad/s.

Time–temperature superposition and related data analysis were carried out with the IRIS software. The kinetic experiments on the phase transition were analyzed with the GEL-PRO software of Mours et al.[12]

Results

Temperature Scans. The dynamic moduli of the LCPUE-1000, measured at a frequency of 10 rad/s and strains of 0.02–0.25, decayed monotonically with increasing temperature; see Figure 2. Both heating and cooling scans with a rate of 1.5 K/min indicate a reversible broad transition from a viscoelastic solid behavior to liquid behavior but did not reveal the exact instant of a first-order phase transition. However, this gradual rheological transition occurs in the same temperature range as the thermal events which are associated with the mesophase isotropization in DSC studies.[1] It should also be noted that there is a small "hysteresis loop" between heating and cooling runs in Figure 2. Moduli are lower on the cooling run than on the heating run. Figure 2 also shows the temperature of the crossover ($G' = G''$) at 132 °C in the heating mode and at 110 °C in the cooling experiment. The difference in the crossover temperatures and the hysteresis are due to the kinetic effect of the mesophase formation. In reference to the crossover temperature at 110 °C, the dynamic moduli G^* of the cooling scan have been
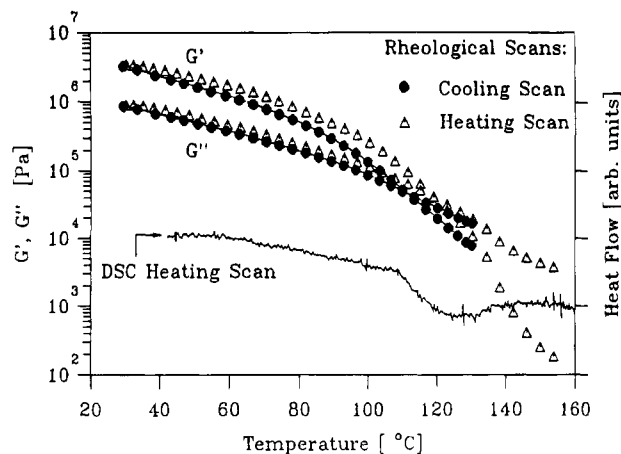
Figure 2. Temperature dependence of the shear moduli G' and G'', compared with the result of the DSC heating scan (lower curve). The circles represent the cooling scan; triangles represent the heating scan. Frequency: 10 rad s^{-1}. Strain varied between 0.2 and 0.0125. Heating and cooling rates were 1.5 K min^{-1} in all experiments; the points belonging to the cooling scan are connected by lines.
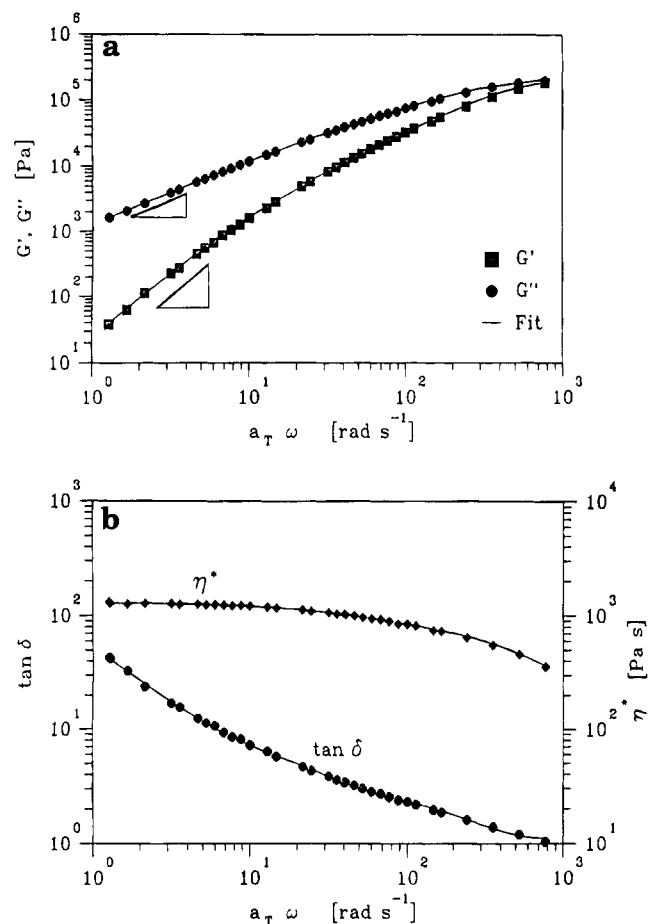
Figure 3. (a) Master curve for frequency scans in the upper temperature region (isotropic phase). Measured shear moduli and fitted curve. Reference temperature: 120 °C. Strain varied between 0.05 and 0.2. The straight lines indicate slopes 1 and 2, respectively. (b) Same as part 3a. Measured complex viscosity (diamonds) and tangent of the loss angle (circles), compared with the fitted curve (solid lines).

studied further for both the viscoelastic liquid (160 °C → 110 °C) and the viscoelastic solid (100 °C → 20 °C) regions.

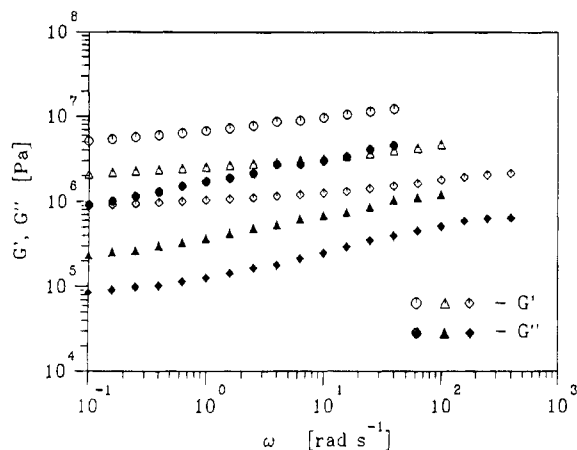**Viscoelastic Liquid Zone.** Figure 3 shows the results of isothermal frequency scans at 110, 120, 140,

Figure 4. Storage and loss moduli according to frequency scans at three different temperatures in the solid state. Circles: 20 °C. Triangles: 60 °C. Diamonds: 100 °C. Strain varied between 0.02 and 0.0125.

and 160 °C. In order to erase annealing history, samples were brought to the isotropic state at 160 °C after each measurement and then back to the experimental temperature. In Figure 3a, a master curve is constructed with a reference temperature of 120 °C. The loss moduli G'' are consistently larger than the storage moduli G'. At low frequencies, the slopes of G' and G'' are 2 and 1, as expected for a viscoelastic liquid, such as a polymer melt. In Figure 3b, the absolute value of complex viscosity η^* ($\eta^* = G^*/\omega$) has a constant value of 10^3 Pa·s at low frequencies and starts to decrease with increasing frequency as the material exhibits shear thinning behavior. Time—temperature superposition is possible (see the master curve at a reference temperature $T_0 = 120$ °C). The temperature shift factors follow the Arrhenius type of temperature dependence with an apparent activation energy of $E_a \approx 60$ kJ/mol.

Viscoelastic Solid Zone. Isothermal frequency scans for various temperatures are shown in Figure 4. The values of the storage moduli G' are always larger than those of the loss moduli G'', as is characteristic for most viscoelastic solids. The slopes of the modulus—frequency plots are much smaller than those in the viscoelastic liquid zone (Figure 3a). A zero slope is approached at low frequencies, as is typical for solids.

Evolution of Viscoelastic Behavior during Physical Gelation. The crossover $G' = G''$ is known to occur not exactly at the gel point[20] but often is close to it. Therefore, it has often been used for rough estimates of the gel point. For LCPUE-1000, the gel point is reached with G'' being about 10 times larger than G', as will be shown below.

The gelation from the viscoelastic liquid to the viscoelastic solid is strongly dependent on thermal history. The evolution of viscoelasticity was studied by heating the sample to 160 °C, where it forms a polymeric melt, followed by quenching to a temperature below 110 °C. Here we chose 106, 101, and 99 °C for the isothermal gelation process. Figure 5a shows the growth of the dynamic moduli versus time at a constant frequency of 0.463 rad/s. The quenching to 99 °C gives the fastest growth of the moduli, indicating the connectivity changes to be caused by physical processes. The observed growth at 106 °C depends on the frequency (Figure 5b), being more pronounced at low frequencies.

In spite of its dependency upon temperature and frequency, the gel point, a liquid/solid transition, can be distinguished by a loss tangent which, at a constant
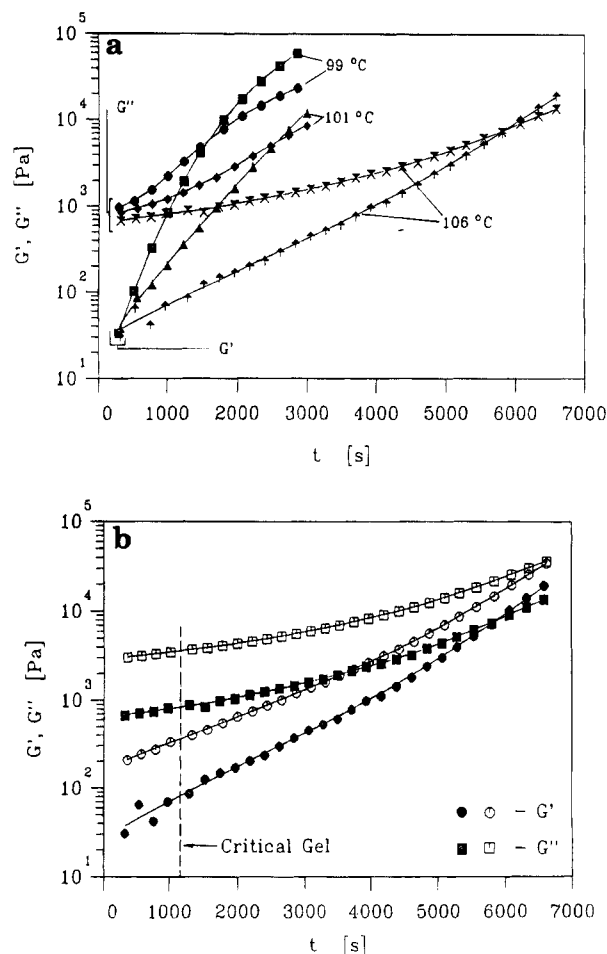

Figure 5. (a) Kinetic study of the phase transition liquid/solid. Evolution of the shear moduli with time at a constant frequency. G': squares, 99 °C; triangles, 101 °C; closed crosses, 106 °C. G'': circles, 99 °C; diamonds, 101 °C; open hourglasses, 106 °C. Strain: 0.02. Frequency: 0.463 rad s^{-1}. (b) Frequency dependence of the solidification process at 106 °C. Two frequencies are shown: 0.463 rad s^{-1} (filled symbols); 2.15 rad s^{-1} (open symbols). The strain was 0.02; the position of the critical gel is indicated by the dashed line in the left part of the figure.
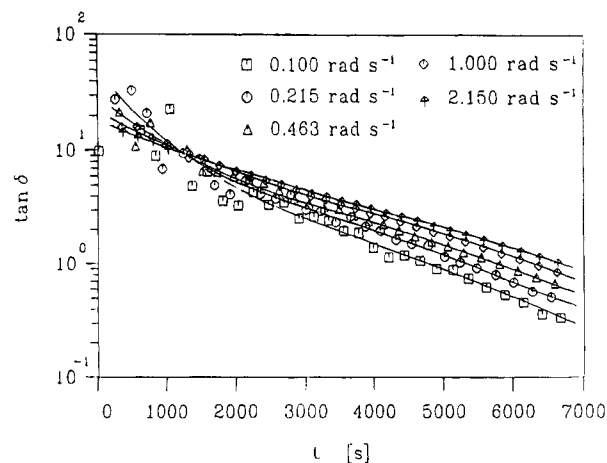

Figure 6. Kinetic study at 106 °C. Strain 0.02, tangent of the loss angle vs time. Frequencies (rad s^{-1}): squares, 0.10; circles 0.215; triangles, 0.463; diamonds, 1.00; closed crosses, 2.15.

temperature, is independent of frequency. Figure 6 shows the tan δ measured at 0.1, 0.215, 0.463, 1.0, and 2.15 rad/s as a function of elapsing time at 106 °C. The crossover of tan δ, which approximately equals 10.1, is
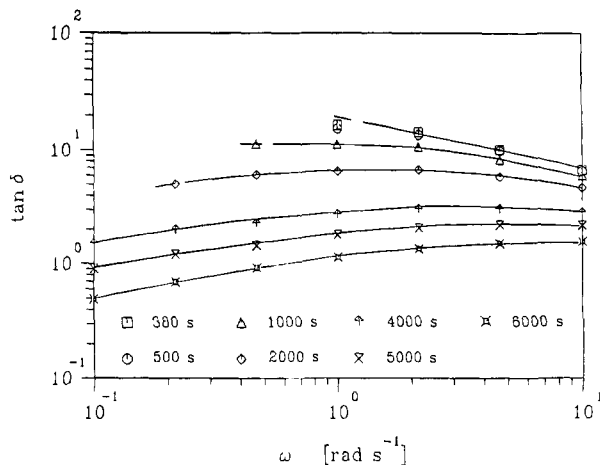
Figure 7. Kinetic study at 106 °C. Strain 0.02, tangent of loss angles vs frequency. Time after starting the observation (s) as indicated in the figure.
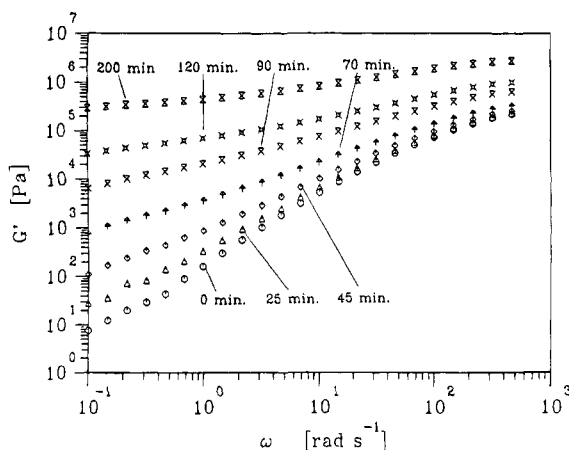

Figure 8. Evolution of the storage modulus during the solidification at 106 °C. Data sets for times up to 200 min after initiating the test.

Figure 9. Five isothermal CFS scans, characterizing the solid/liquid transition. The arrows indicate the evolution of the loss tangent in time for the isothermal scans. For three experiments (at 125, 136, and 150 °C), dashed lines mark for the whole frequency window the upper and the lower limit of the range, in which tan δ did change. The temperatures were increased in the following sequence: triangles, 125 °C; diamonds, 132 °C; circles, 136 °C; closed crosses, 143 °C; open hourglasses, 150 °C.

observed as frequency independent. The corresponding time is 1090 ± 20 s for the formation of the critical gel. As the time passes, the viscoelastic liquid has increased its elasticity (Figure 7). It is further substantiated by the steady increase of the storage modulus G' (Figure 8). At the critical gel point, the relaxation exponent n equals 0.937. From eq 2, the value of the gel stiffness S is calculated as 107 Pa s^n.

Softening of the Solid State. In the reverse process, the physical gel is "melted" by the isotropization of the mesophase, resulting in a viscoelastic transition from solid to liquid. Five isothermal CFS scans at 125, 132, 136, 143, and 150 °C are given in Figure 9. The change of loss tangent versus time is indicated by the arrows in the figure. As the sample is heated above 132 °C, tan δ increases continuously with time, indicating the development of the terminal zone behavior, as is typical for an isotropic fluid. At 125 °C, the decrease of the tan δ values with time shows an increase of the elasticity by annealing.

Discussion

The physical network formation of the segmented copolymer results in a distinct change from a viscoelastic liquid to a viscoelastic solid. This is accompanied by a significant rise in the storage and loss moduli. Submicrometer-sized mesophasic domains are formed and act as physical cross-links. The rheological hysteresis in
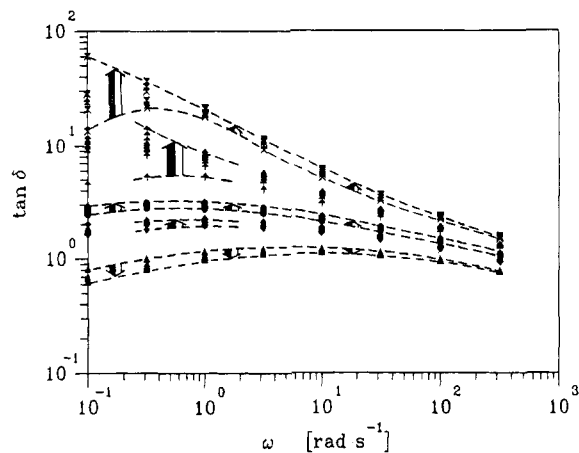
Figure 2 is due to the kinetic effects of ongoing structural reorganization.

In the high-temperature liquid phase, time–temperature superposition behavior shows that the morphology of the polymer remains the same upon cooling from 160 to 110 °C. This does not necessarily imply the existence of a single phase, since even binary separated phases have been reported to obey time–temperature superposition.[13,14] Furthermore, in the cooling scan from 160 °C, a kinetically controlled gelation takes place at temperatures below 110 °C.

The CFS scans in the heating mode show that the isotropization of the mesophase occurs at a higher temperature than its formation. The development of the terminal zone corresponds to the broad isotropization, as observed by DSC.[1] However, in Figure 2, the softening effect of LCPUE-1000 before the isotropization is observed by the gradual decrease of the dynamic moduli. This is largely due to the increased mobility of the soft segments with increasing temperature, and other possible structural changes resulting from the loss of sample connectivity.

A viscoelastic liquid/solid transition caused by physical cross-linking has been identified by the rheological method, and a critical gel was observed at 106 °C. For LCPUE-1000, we find the relaxation exponent $n = 0.94$, a relatively high value, compared with other critical gel data.[15-17] In chemically cross-linking systems, relaxation exponents are between 0.5 and 0.7.[7-9,18] In physically cross-linking systems with crystalline units as hard segments,[10,11] the relaxation exponents are usually between 0.11 and 0.13, with the exception of the PVC plastisol system, which yields a value of 0.8.[19] The relaxation exponent and the gel stiffness of 107 Pa s^n indicate a very soft structure with a high degree of internal mobility in LCPUE-1000.

Conclusion

A broad viscoelastic solid/liquid transition is observed by rheology. A mechanical hysteresis and a crossover ($G' = G''$) temperature difference between heating and cooling scans are due to the kinetically controlled transition. The CFS method has been applied to

identify the viscoelastic transition at 106 °C and shows the existence of a critical gel, which obeys a power law. The quantitative analysis yields values for the gel stiffness and the critical exponent, which indicate a soft gel structure with a high degree of mobility.

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MA9410779