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DYNAMIC VISCOELASTIC MEASUREMENTS OF PVC GELS

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Abstract—This paper deals with dynamic viscoelastic measurements on poly(vinyl chloride)/dioctyl phthalate gels. The curves of the storage modulus, G', vs temperature (at a frequency of 0.1 Hz) show a characteristic gel-like plateau at low temperatures. Using the theory of rubber elasticity, the molecular weights between the associations that constitute the structure of the gel, $\bar{M}_e$, are obtained for different concentrations and for samples of different molecular weight. It is seen that there is an effect of molecular weight on $\bar{M}_e$, which is not the normal behaviour for other polymer gels. The frequency dependence of G' and G'' is studied at various temperatures for the range 10^{-2} Hz to 10^2 Hz; the slope of G' vs frequency increases from zero, at gel behaviour temperatures, to values tending to 2, at temperatures above the fusion of the gel and low frequencies. On the other hand the loss tangents show minima at intermediate frequencies, a feature characteristic of entangled polymer systems. We have also carried out complementary measurements on a steady rotation viscometer, the results being in accordance with the values of dynamic complex viscosity.

INTRODUCTION

Gels are formed in polymer/diluent systems by linkages constituted by association of separated loci. In some cases, such as gelatin/water and agar/water the nature of the linkages remains difficult to elucidate; in the case of poly(vinyl chloride) in various solvents, polyacrylonitrile in dimethylformamide and atactic polystyrene in carbon disulphide, the junction points are probably formed by crystals.

Because of the commercial importance of poly(vinyl chloride), PVC, and the facility of this polymer to form gels with plasticizers, much of the work on physical properties of gels refers to these systems. The work published by Walter in 1954 [1] dealt with results of the modulus of elasticity of rather soft PVC gels; more recently, Yang and Geil [2] analyzed the morphology and properties of PVC/solvent gels, suggesting that molecular entanglements and hydrogen bonding, rather than crystals, were responsible for gel formation.

In spite of the increasing importance of dynamic viscoelastic measurements in polymer science, this technique has not been used to analyze the rheological properties of PVC based gels. Only the work by Nakajima *et al.* [3–5], concerning the analysis of gelation and fusion mechanisms of PVC plastisols by means of dynamic viscoelastic measurements, has been published. However, in the case of not so well-known systems such as agar–agar gels, PS/CS_2 gels, rod-like polymer gels, DNA gels and actin gels, reports on dynamic viscoelastic behaviour have been published [6–10].

The work presented here deals with the results of measurements of the storage modulus G', loss modulus G'', loss tangent tg δ and complex viscosity η^*, carried out for temperature scan and isothermal frequency scan conditions. Complementary rheological data at temperatures above the fusion of the gel are also presented.

EXPERIMENTAL

Samples

Three commercial suspension polymerized PVC (from Industrias Químicas Asua, Bilbao, Spain) MS-2209, MS-2210 and MS-2212, with molecular weights $\bar{M}_v = 40{,}600$, 51,100 and 62,500 respectively, were used to prepare gels with dioctyl phthalate, DOP, as plasticizer. The fine particles of PVC were dispersed in DOP and the temperature was raised to 160°C and kept at this temperature with gentle stirring for 30 min, to assure the fusion and homogenization of the system; then the solution was allowed to cool, obtaining the gel at room temperature (25°C). For samples prepared under these conditions and for storage times longer than 2 hr, no ageing effect was observed in the measured viscoelastic properties. Table 1 shows the gel compositions used in our work.

Dynamic viscoelastic measurements

The Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) was used in the shear mode. In order to obtain the storage modulus $G'(\omega)$, the loss modulus $G''(\omega)$, the loss tangent tg δ (ω) and the complex viscosity $\eta^*(\omega)$ as a function of the frequency, ω, at different temperatures, a new program, which allows measurements for 16 frequencies at each temperature, was developed [11].

Rotational flow measurements

Two kinds of experiments were carried out in a two cylinder type Brabender Viscotron viscometer. In the first

Table 1. Gel compositions. C is weight percent of PVC

MS-2209 $\bar{M}_v = 40{,}600$ $C(\%)$	MS-2210 $\bar{M}_v = 51{,}100$ $C(\%)$	MS-2212 $\bar{M}_v = 62{,}500$ $C(\%)$
15	15	15
20	20	20
25	25	25
30	30	30
35	35	35
40	40	40
45	45	45
55		

set of experiments, the homogeneous systems were poured in the viscometer at 160°C; the rotating cylinder was acting at a constant velocity, corresponding to a shear rate of $0.25\,\mathrm{sec}^{-1}$. While the temperature decreased sequentially, the viscosity, η, was recorded, allowing analysis of the recrystallization process.

In the second type of experiment, flow curves of the homogeneous solutions were obtained at various temperatures and shear rates. The results were adjusted to power law model and Arrhenius like equations.

RESULTS

Figures 1, 2 and 3 show the storage modulus, G', for various molecular weights and concentrations and loss tangent tg δ for various molecular weights, taken at a frequency of 0.1 Hz, as a function of temperature. At temperatures above the fusion of the system (which correspond to values tg $\delta > 1$), it was very difficult to obtain reliable data with DMTA viscoelastometer, so the isothermal experiments were carried out at temperatures below that at which the fusion process began. The plots of G' and tg δ for isotherms ranging from 25°C to 120°C and frequencies from 10^{-2} Hz to 10^{2} Hz are presented in Fig. 4 (Sample MS-2209-25%) and Fig. 5 (Sample MS-2209-25%).

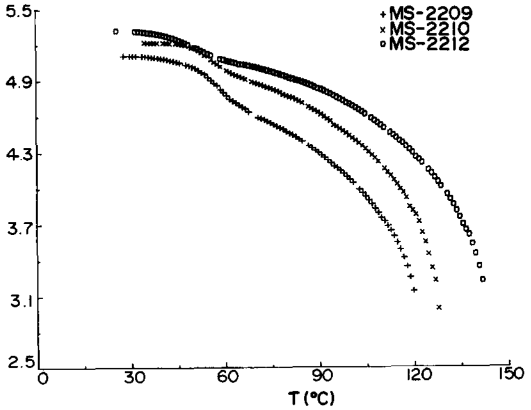

Fig. 1. Storage modulus as a function of temperature for gels of different molecular weight PVC. Polymer weight concentration $C = 25\%$.

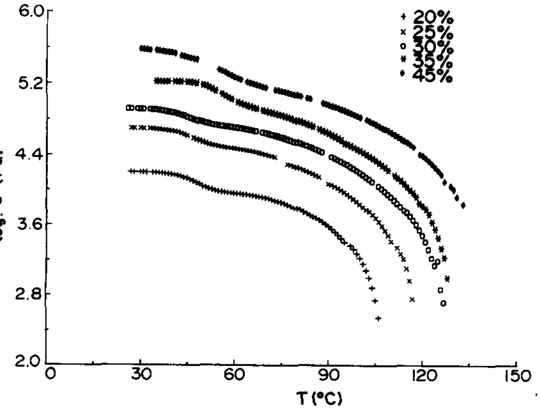

Fig. 2. Storage modulus vs temperature for gels of different concentrations of MS-2209 PVC.

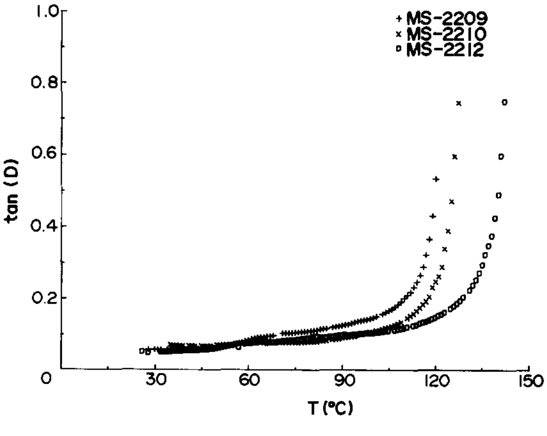

Fig. 3. Loss tangent as a function of temperature for gels of different molecular weight PVC. Polymer weight concentration $C = 25\%$.

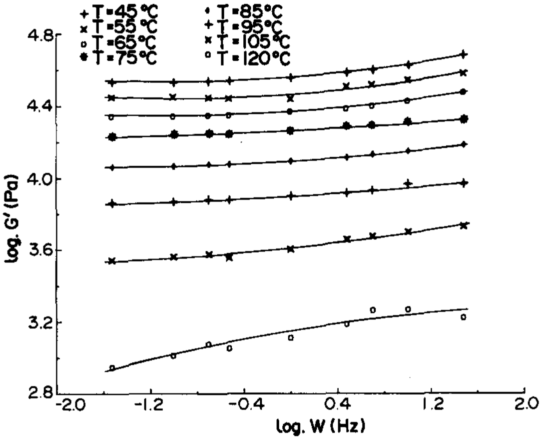

Fig. 4. Storage modulus against frequency at different temperatures for MS-2209-25% gel.

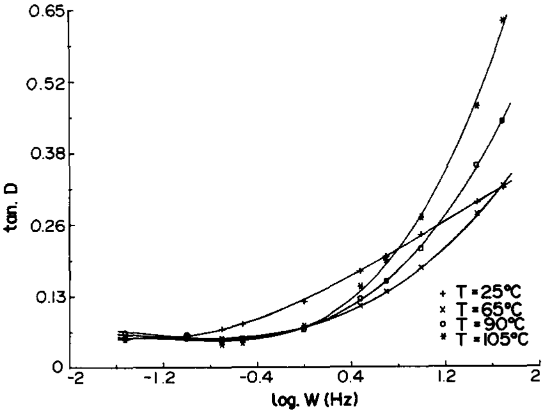

Fig. 5. Loss tangent vs frequency at different temperatures for MS-2209-25%.

In order to compare the behaviour of the storage modulus G' and the loss modulus G'' at low temperatures and temperatures close to fusions, Figs 6 and 7 include the plots of these functions at 27°C and 140°C for sample MS-2209-45%.

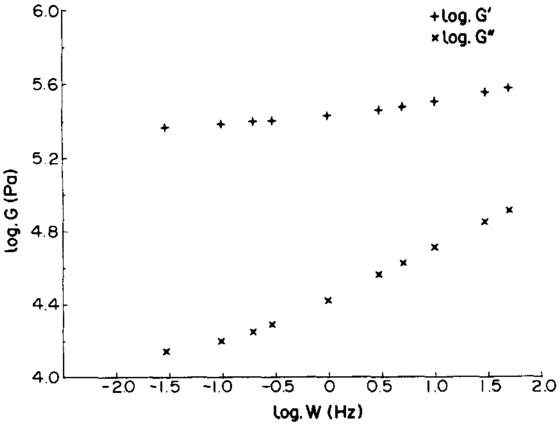

Fig. 6. Storage and loss moduli as functions of frequency at 27°C. Sample MS-2209-45%.

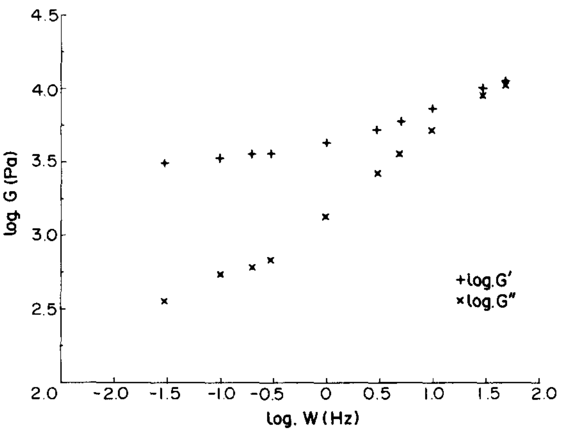

Fig. 7. Storage and loss moduli as functions of frequency and at 140°C. Sample MS-2209-45%.

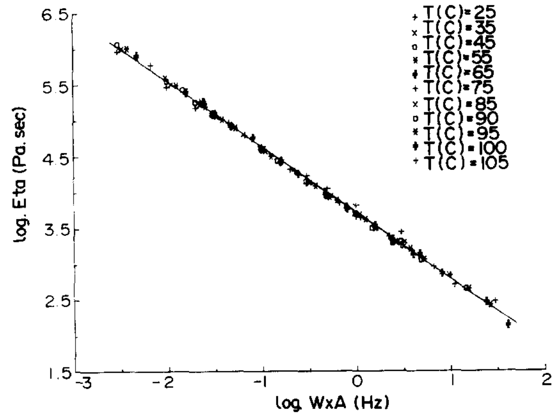

Fig. 8. Master curve of complex viscosity against frequency. The reference temperature is $T_r = 105$°C and the sample MS-2209-25%.

The complex viscosity η^* is plotted against frequency at different temperatures. In all the cases, the curves were superposable in the range of temperatures used in the DMTA and consequently master curves can be obtained, as presented in Fig. 8 for MS-2209-25%. The corresponding shift factors A can be represented against (temperature)$^{-1}$ as shown in Fig. 9.

The data of the viscosity obtained at $\dot{\gamma} = 0.25$ sec^{-1} in the rotational viscometer during the cooling process of the solutions are presented in Fig. 10. These

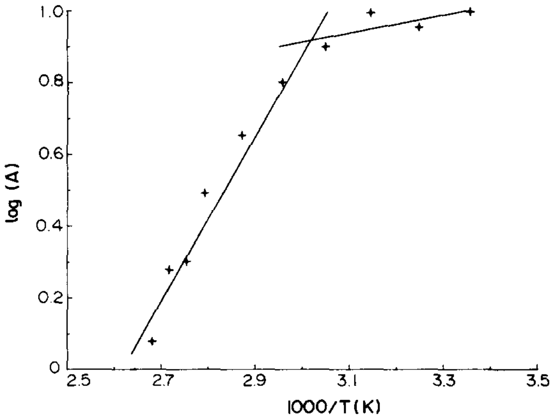

Fig. 9. Shift factors A used in Fig. 8 represented against (absolute temperature)$^{-1}$.

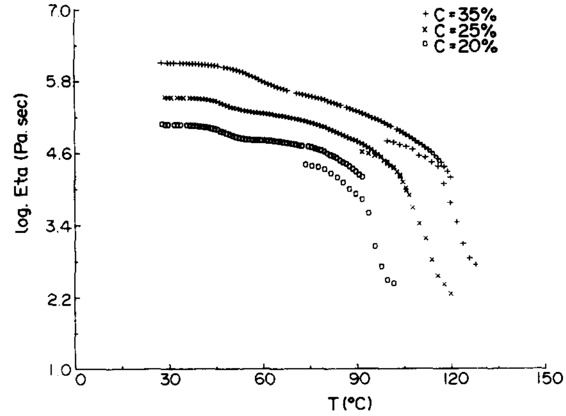

Fig. 10. Complex viscosity, taken at 0.1 Hz, and steady state viscosity, at 0.25 sec^{-1}, as a function of temperature. Higher temperature curves correspond to steady data. PVC is MS-2209.

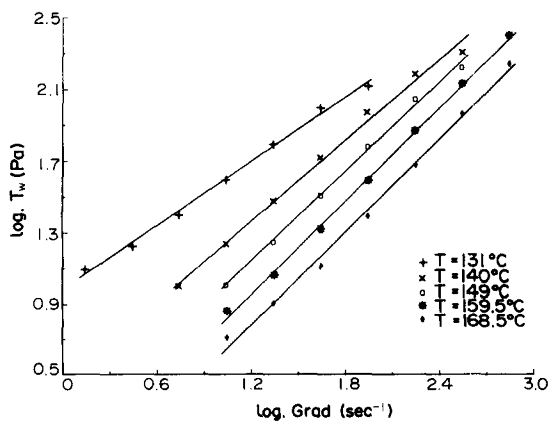

Fig. 11. Flow curves—shear stress vs velocity gradient—for MS-2209-25%. Sample, obtained in rotational steady-state viscometer.

data are compared with the complex viscosities obtained from DMTA in a heating process at a frequency of 0.1 Hz.

Concerning the flow curves of homogeneous solutions, the results for the sample MS-2209-25% are shown in Fig. 11. When applying the superposition method to obtain the master curve, we have excluded the temperature $T = 131°C$ and only the curves that possess the same slope (same exponent on $\tau = K\dot{\gamma}^n$ equation) are included in Fig. 12. Similar results were obtained for the other samples, noting that only above a certain temperature were the curves superposable. The values of the activation energies of flow, obtained from Arrhenius like plots of the shift factor A, are presented in Table 2.

DISCUSSION

The results presented in Figs 1 and 2 are similar to those obtained by Nakajima *et al.* during their second heating scan, after the sample was maintained at 200°C and then cooled (Fig. 9 of Ref. 5). It is seen that at low temperatures the gel keeps its structure, formed probably by micellar crystal conexions; at high temperatures however the gel fuses and the storage modulus decreases rapidly whereas the loss tangent increases abruptly (Fig. 3). It is also worth pointing out that, as can be seen clearly from Fig. 1, there are two plateau zones. This fact, not previously reported for gels, as well as the analysis of the fusion temperature are the subjects of another work [12] and will not be discussed here.

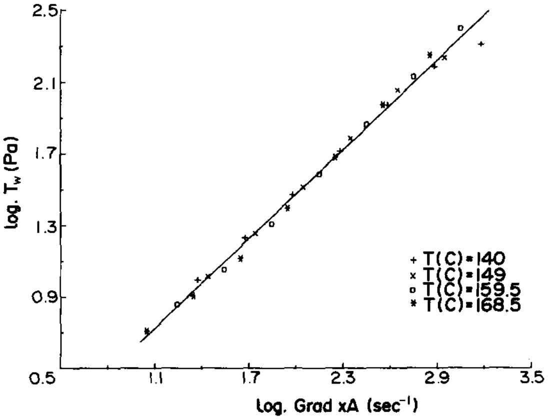

Fig. 12. Master curve of flow curves of Fig. 11, excluding $T = 131°C$. Reference temperature = 168.5°C.

Table 2. Activation energies of flow obtained from steady state rotational measurements

PCV(MS-2209)/DOP	
C(%)	E_a(kJ/mol)
15	52.5
20	61.7
25	76.8
30	95.3

As can be seen from Fig. 1, the value of G' in the first plateau region, $G'e$, increases with the molecular weight and more severely with the concentration, following the equation

$$\log G'e = 0.6 + 3.9 \log(C \cdot A) \qquad (1)$$

as obtained from Fig. 13. In this equation, C is the polymer concentration and A values are 0.79, 0.86 and 1 for MS-2209, MS-2210 and MS-2212, respectively.

This result is in accordance with the concentration dependence of the pseudo-equilibrium modulus for PVC gels reported in the literature [13]. We can use the values of $G'e$ in the expression for the modulus in the theory of rubber elasticity:

$$G = \frac{CRT}{\bar{M}_e}\left(1 - \frac{2\bar{M}_e}{M}\right) \qquad (2)$$

where $\bar{M}_e$ represents the molecular weight between the associations that constitute the functions of the structure of the gel.

For a given polymer at a given concentration and temperature, the modulus should depend only on $\bar{M}_e$ and, therefore, according to Eqn 2 the plots of $G'e$ vs $1/M$ should give a straight line from which $\bar{M}_e$ can be determined. In Fig. 14 we present these plots for different concentrations. The data do not fit a straight line, so we suggest that in our case the three different molecular weight samples of PVC act as if they were chemically different polymer species, giving

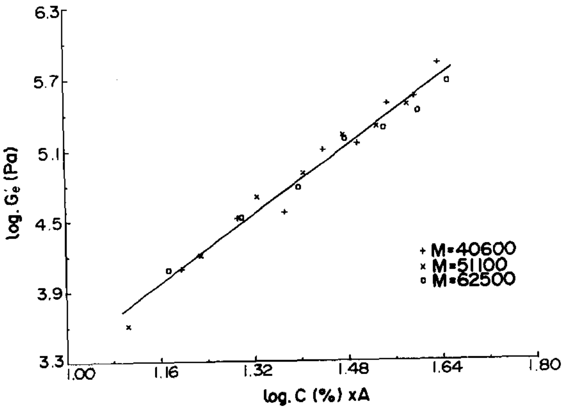

Fig. 13. The values of G' in the first plateau region, $G'e$, (see Figs 1 and 2) represented against the concentration for the three molecular weights.

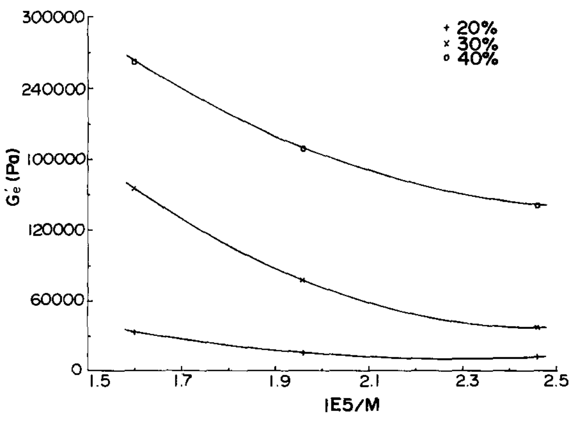

Fig. 14. Plots of $G'e$ vs the inverse of the molecular weight, at various concentrations.

Table 3. Values of the molecular weight between associations, $\bar{M}_e$, obtained from Eqn 2 at 30°C

(MS-2209): $\bar{M}_v = 40{,}600$

$C(\%)$	20	25	30	35	40	45	55
$\bar{M}_e$	19,400	18,450	18,600	16,020	16,060	13,250	10,290

(MS-2210): $\bar{M}_v = 51{,}100$

$C(\%)$	15	20	25	30	35	40
$\bar{M}_e$	24,900	23,730	21,510	20,270	17,930	17,340

(MS-2212): $\bar{M}_v = 62{,}500$

$C(\%)$	15	20	25	30	35	40	45
$\bar{M}_e$	28,460	25,990	24,380	19,050	18,690	16,920	13,040

rise to different values of $\bar{M}_e$. This is not the case for different molecular weight samples of polystyrene when forming gels with CS_2, as pointed out recently [14]. In Table 3, we summarize the values of $\bar{M}_e$ for the different samples, obtained directly from equation 2 at $T = 30$°C.

Although for undiluted and concentrated solutions of polymers, the literature contains many data of frequency sweep measurements (including the case of PVC [15]), published results on frequency dependence of dynamic viscoelastic functions are scarce for gels. We must call attention to the work by Nishinari [6] about tensile storage and loss modulus on agar–agar gels, the work by Clark *et al.* on PS/CS_2 gels [7] and Sato *et al.* [10] on actin gels and the work by Winter *et al.* (16–17] concerning frequency sweep measurements of polyurethanes and polydimethylsiloxanes at the gel point.

From Figs 3 of references 16 and 17, we can obtain a general idea of the frequency behaviour of G' and G''. At low frequencies, before network formation, the sample exhibits liquid behaviour characterized by $G' \propto \omega^2$ and $G'' \propto \omega$; however, as network formation begins, the dependence of G' on ω decreases and, after the network is completed, G' is independent of frequency ($G' = \text{constant}$). The same behaviour is observed (Figs 1–5 of reference 7) for PS/CS_2 gels. Our results (Figs 4, 6 and 7) show the same trend and it is interesting to note that even at high temperatures—120°C for MS-2209-25% or 140°C for MS-2209-45%—corresponding to a zone where the storage modulus decreases rapidly with temperature (Fig. 1) and fusion of the gel begins, the dependence of G' on frequency is still very slight. However, comparing Figs 6 and 7, we see that at 140°C the viscoelastic behaviour is different from that at room temperature; as the frequency increases, G'' tends to overcome G' approaching liquid-like behaviour. The operation limits of our dynamic viscoelastometer make it impossible to go to higher temperatures.

Regarding the loss tangent results, Fig. 5 suggests the presence of a minimum at intermediate frequencies. This is a manifestation of solid-like behaviour. Minima corresponding to entanglements network in undiluted and concentrated solutions of random coil polymers, are typical [18].

Applying the superposition principle, the complex viscosity can be analyzed over a wider range of frequency, as we can see in Fig. 8 where nearly 10^{-3} Hz are attained. The behaviour observed is the general rule also for the other samples. The first observation we can make is that the slope of $\log \eta^*$ vs $\log \omega$ plot is -1. This strong dependence of the viscosity on frequency is characteristic of solids, indicating the presence of a yield stress; it has been observed, for instance, in thermotropic polymers [19, 20], small molecule smectic liquid crystals [21] and highly particulate filled polymer systems [22]. In the case of PVC, Picón *et al.* [15] obtain slopes for $\log \eta^*$ vs $\log \omega$ plots close to -1 at 160°C and yield stresses were observed in our laboratory at temperatures below a critical temperature which depends on molecular weight [23].

This solid-like character is confirmed by the dependence of the shift factor, A, upon (temperature)$^{-1}$. As seen from Fig. 9, the data can be adjusted to two Arrhenius equations, giving rise to an activation energy of $E_a = 4.2$ kJ/mol at low temperatures and $E_a = 42$ kJ/mol at temperatures above 60°C. The results are in contradiction to those obtained for solutions and undiluted random coil polymer systems, where the activation energy decreases as temperature increases (William–Landel–Ferry equation). The very low dependence of the complex viscosity on temperature it is confirmed in Fig. 10 where a heating temperature scan of η^* obtained at $\omega = 0.1$ Hz is compared with the data of viscosity, η, at $\dot{\gamma} = 0.25\ \text{sec}^{-1}$ obtained in a steady state rotational viscometer while cooling took place. The correspondence of the data of both measuring systems is rather good.

Only above temperatures where tg $\delta > 1$, at frequency 0.1 Hz (see Fig. 3), or $G'' > G'$, we can be sure that a homogeneous flow (liquid behaviour) occurs. In this sense, the steady state rotational results in Fig. 11 are confirmative: the flow curve corresponding to $T = 131$°C is not superposable and only at temperatures of $T = 140$°C and above a reasonably good master curve (Fig. 12) can be obtained. The slope $n = 0.8$ of the $\log \tau$ vs $\log \dot{\gamma}$ plot can be considered in the range of values for usual thermoplastics well above T_g.

The values of the activation energies of flow, obtained from shift factor data, are presented in Table 2. The influence of the concentration of polymer on these values is of the same type as observed for polymers like polybutadiene and polystyrene [24]. Nevertheless a free volume additivity equation proposed recently [25] for polyarylate/*m*.cresol systems, does not hold for PVC/DOP solutions.

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