Polymer Bulletin 53, 367–375 (2005)
DOI 10.1007/s00289-005-0345-x

Polymer Bulletin

Calorimetric and rheological studies of 12-hydroxystearic acid / digycidyl ether of bisphenol A blends

Jean Pascal Eloundou[1](✉), Emmanuel Girard-Reydet[2], Jean-François Gérard[2] and Jean-Pierre Pascault[2]

[1] LMMC, Ecole Nationale Supérieure Polytechnique, B. P. 8390 Yaoundé, Cameroun
Fax: +237-222-45-47, E-mail: jp_eloundou@yahoo.fr

[2] LMM/IMP, UMR CNRS # 5627, Institut National des Sciences Appliquées de Lyon, 20 Avenue Albert Einstein, 69 621 Villeurbanne cedex, France

Received: 11 December 2004 / Revised version: 27 January 2005 / Accepted: 27 January 2005

Summary

Above a concentration c^* close to *0.3 wt%*, blends of 12-hydroxystearic acid (HSA) with diglycidyl ether of bisphenol A (DGEBA) prepolymer mixed at *80°C* give thermally reversible physical gels (organogels) on cooling.

According with the literature, the turbidity of the gels indicates fibres of rectangular cross-sectional shapes. The slope of the linear melting heats versus concentration is equal to the melting heat of the pure HSA ($-182 \pm 4\ J.g^{-1}$).

The blends are gels as the elastic modulus G' is about ten times larger than the loss one G'' and G' is practically independent of the frequency at a given concentration.

The sharp variation of the temperature of the endothermic peak T_{peak}, of the time to reach the rubbery plateau t_r, of the exponent Δ ($G' \propto \omega^{\Delta}$) and of the limiting strain γ_l of the linear viscoelastic domain below *2.5 wt%*, is attributed to smaller crystallites in the blend.

At a given frequency, G' follows a scaling law with the concentration ($G' \propto c^{\beta_1}$), the scaling exponent β_l being equal to 3.87 ± 0.02 at $1\ rad.s^{-1}$. This indicates that the gel structure is independent of the concentration.

Introduction

Low molar mass molecules "gelators" in a semidilute range of concentration are known to gel some organic solvents and give thermoreversible plastic materials or physical gels [1]. Among these, the 12-hydroxystearic acid (HSA) is of special interest because of the exceptionally large variety of solvents, which can be gelled at small concentrations (less than *1wt%*) and its use in industrial applications (detergents and lubricating greases). The physical gels of HSA were obtained with various solvents such as carbon tetrachloride [2,3], fluorobenzene [4], octane [4], benzene [4,5], nitrobenzene [4-6], hexafluorobenzene [4-6], cyclohexane [4-7], toluene [6], chloroform [7], methanol [7], soybeanoil [8]. Above a critical concentration or gelation threshold c^* (for example *0.345 wt%* in nitrobenzene [5]), the heated solution forms a gel upon cooling. The gels formed are strong gels as they break upon large deformation and can be re-formed only after a new gelation cycle. The organogel may be transparent (in benzene [4,5], toluene [6] or soybeanoil [7,8]) or less or more turbid in other solvents (depending on the concentration and the nature of the solvent [4-8]). Gelation can be promoted by pressure [3]. The addition of small amounts of alkali metal ions, which can be supplied in the form of alkali metal salts of HSA, lowers the gelation threshold, increasing the turbidity of soybeanoil/HSA gels. It also promotes the gel stiffness, inducing more mechanically durable gels [8].

To understand the mechanisms which involve gelation, these organogels has been studied by numerous techniques: electron microscopy [7-9], infrared absorption spectroscopy [2,7,8,10], optical measurements [11,12], wide angle X-ray scattering [4,5,11,12], small angle neutron scattering [4-6], small angle X-ray scattering [5] differential scanning calorimetry [5], nuclear magnetic resonance [6,7]. To summarise the observations of these authors, HSA fibres in hydrocarbon gels involve H-bonds forming zigzag sequences along the fibre axis and head to head contacts within the orthogonal plane between carboxylic acid groups. Fibres are rigid and very long (up to micrometers), and their cross-sectional shapes depend on the solvent type. They are interconnected in crystalline monoclinic domains. The cross-sectional shapes of the fibres were found to be square in transparent gels and rectangular in turbid gels [4]. The crytallinity and the melting temperature increase with the turbidity.

The physical gels have been studied by many authors using dynamic rheology [5,6,13-16]. It was found that they exhibit a gel behaviour as the elastic modulus G' is greater than the loss modulus G'' while for a Newtonian liquid, G'' is larger than G'. In the case of HSA/hydrocarbons and other physical gels [6,13,15], G' was found to be about ten times greater than G''. The linear viscoelastic domain where the dynamic moduli are independent on the strain is restricted to small strains [6,14]. So the gel is fragile.

While studying interpenetrating chemical and physical gels, it has been observed that a physical gel is obtained by dissolution of small amounts of poly(vinyl chloride) ($c = 3.25$ *wt%*) in digycidyl ether of bisphenol A [17]. The gelation phenomenon was shown by the intersection of the loss factor $\tan\delta$ versus time curves measured isothermally at different frequencies as already found for chemical gels [18-20].

Recently, attempts have been made to gel others liquid, particularly epoxies, with 12-hydroxystearic acid. The aim of this work is then to present some results obtained in calorimetric and rheological studies of 12-hydroxystearic acid / digycidyl ether of bisphenol A (HSA/DGEBA) organogels.

Experimental part

Preparation of the blends

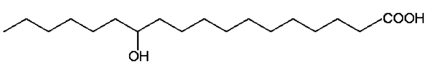
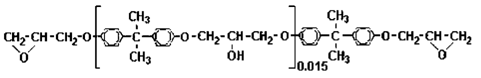
A DGEBA prepolymer with low degree of polymerization ($n = 0.015$), supplied by Dow Chemicals (DER330), was used. The HSA, supplied by Fluka, is of purity grade *70* to *80%*, the impurity being the stearic acid. The appropriate mass of HSA (concentration c of HSA from *0.3 wt%* to *5 wt%*) is dissolved in the DGEBA heated at *80°C* under mechanical stirring. The characteristics of the products are given in Table 1. All products were used as received.

Differential Scanning Calorimetry

Differential scanning calorimetry analysis (DSC) was carried out using a Mettler TA3000 apparatus under argon atmosphere. Samples of mass between *30 mg* and

40 mg were sealed in aluminium spans with pierced lids and tested in the dynamic mode from *-90°C* to *100°C* at *10 degrees.min*$^{-1}$. The glass transition temperature (onset) T_g, the temperature of the peak T_{peak} and the enthalpy of melting ΔH are measured.

Table 1. Characteristics of the products

Product	Formula	Supplier	Molar mass (g.mol^{-1})	Melting point (°C)
12-Hydroxystearic acid (HSA)		Fluka	300.49	75 - 80
Diglycidyl ether of bisphenol A (DGEBA (*n* = *0.015*))		Dow Chemicals DER 330	348.5	

Rheology

Dynamic mechanical measurements were performed with a Rheometrics Dynamic Analyser apparatus (RDA II) from Rheometrics equipped with parallel plates of *40 mm* diameter with a gap of about *1.5 mm*.

The mixture placed between the plates is heated up to *80°C* and the time sweep experiment begins at the angular frequency $\omega = 1\ rad.s^{-1}$ while the temperature decreases to *30°C*. Then the experiment continues isothermally at *30°C* until the elastic modulus *G'* remains constant (rubbery plateau). Because of the fragility of the gel, the value of the strain is small, about $\gamma = 0.07\%$ ($\gamma = 0.1\%$ for concentration below *2.5 wt%*).

When the rubbery plateau is reached, the frequency sweep experiment begins with the same strain from $\omega = 0.1\ rad.s^{-1}$ to $\omega = 100\ rad.s^{-1}$ followed by a strain sweep experiment from $\gamma = 0.001\%$ to $\gamma = 100\%$ at the angular frequency $\omega = 1\ rad.s^{-1}$. The strain sweep experiment allows to verify that the time sweep and frequency sweep experiments have been done in the linear viscoelastic domain.

To check the reversibility of the gelation phenomenon, a temperature cycle was adopted, as reported in Figure 1. A frequency sweep experiment at *1 rads.s*$^{-1}$ was performed on cooling from *80°C* to *28°C* followed by a time sweep experiment and another frequency sweep experiment on heating from *28°C* to *80°C*. The temperature rate was about *2.4 degrees.min*$^{-1}$ and the strain varies from *50%* in the liquid state to *0.07%* in the solid state. Figure 1 represents the results obtained for $c = 3$ *wt%*. It is observed that the shapes of the elastic moduli measured on cooling and heating are quite the same. This behaviour shows the thermoreversibility of the gelation phenomenon.

Results and discussion

Gel aspects

The blend, which is transparent and homogeneous at *80°C*, gels under cooling. Below $c = 0.3$ *wt%*, no gelation has been observed, even after several weeks. Then it has been assumed that the critical concentration or gelation threshold is close to $c^* = 0.3$ *wt%*. This value is comparable with that found in the case of HSA/nitrobenzene blend (*c* = 0.345 wt%*). A very turbid gel is obtained for concentrations greater than *c = 2.5 wt%*. At lower concentrations, the gel becomes less and less turbid. Considering the observations of Terech [4] concerning the cross sectional shape of the fibres, it may be expected that these are rectangular as the gel is turbid.

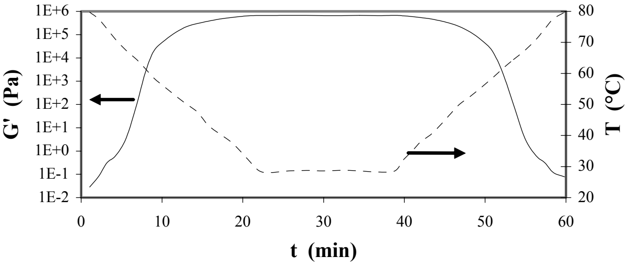


Figure 1. Primary Y-axis: *G'* recorded during temperature sweep experiment at *3 wt%*. Secondary Y-axis: Temperature profile.

Calorimetric results

Figure 2 shows examples of thermograms obtained in DSC. The thermogram of the HSA alone (without DGEBA) owns two peaks. These peaks can be attributed to the melting of the HSA for the high temperature one and to the melting of the stearic acid impurity (*20 – 30%*) for the low temperature one. The value of T_{peak} (76 ± 2 *°C*) of the highest temperature peak is in good agreement with the value of the melting temperature given by the supplier (*75 – 80°C*).

The curves show a drop due to glass transition followed by an endothermic peak corresponding to the melting of the gel. The glass transition temperatures T_g, the melting heats ΔH and the temperatures of the peak T_{peak} are reported in Table 1. The values of T_g are close to that of pure DGEBA. The evolutions of ΔH and T_{peak} are represented versus concentration *c* in Figure 3. Their values depend on the concentration *c*.

The curve ΔH versus *c* exhibits a linear shape with a slope $-185.7\ J.g^{-1}$ very close to the melting heat of the pure HSA ($-182 \pm 4\ J.g^{-1}$). Indeed, the melting of the blend results from the supramolecular organisation of the HSA in the DGEBA.

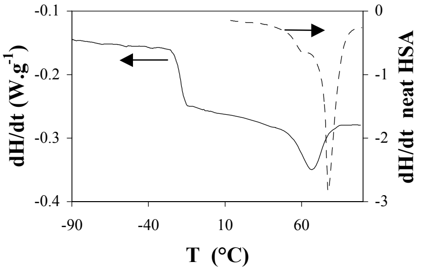


Figure 2. Primary Y-axis: thermograms of HSA/DGEBA blends at *5 wt%*. Secondary Y-axis: thermogram of HSA alone.

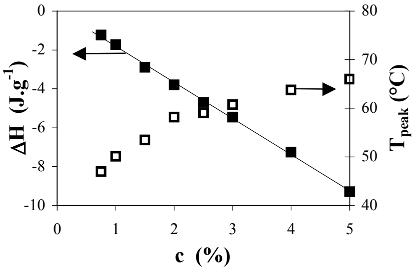


Figure 3. Enthalpy of melting and temperature of the endothermic peak of HSA/DGEBA blends versus concentration.

Table 2. Calorimetric and rheological parameters of 12-hydroxystearic acid / digycidyl ether of bisphenol A (HSA/DGEBA) blends

C *(wt%)*	T_g (°C)	T_{peak} (°C)	ΔH (J/g)	t_r (min)	G' (x 10^3 Pa)	Δ	γ_l
5.00	-22.47	65.97	9.30	20	4080.0	0.017	0.03
4.00		63.72	-7.25	20	1410.0	0.005	0.14
3.00		60.74	-5.46	22	609.0	0.014	0.47
2.50		59.00	-4.70	104	252.0	0.039	1.64
2.00	-22.32	58.13	-3.80	300	111.0	0.045	6.71
1.50		53.50	-2.90	535	44.8	0.041	19.10
1.00	-22.88	50.16	-1.73	900	6.8	0.067	
0.75		47.00	-1.24			0.073	

More complicated is the evolution of T_{peak} as function of c. From $c = 0.75$ *wt%* to $c = 2.5$ *wt%*, a sharp increase of T_{peak} is observed. Above $c = 2.5$ *wt%* the increase of T_{peak} is less pronounced with a possibility to reach a plateau value. This behaviour has been observed by Terech et al [6] for HSA/dodecane and HSA/toluene gels. They found that HSA/dodecane gels, for which the fibres exhibit rectangular cross-sectional shapes, have melting temperatures higher than those of HSA/toluene gels, which are less turbid and exhibit square cross-sectional shapes. In the case of cholesteryl 4-(2-anthryloxy) butyrate/dodecane gels, the sharp increase of T_{peak} appears to include sol-gel formation [21]. At all concentrations, a small amount of the gelator (solubility limit) remains free in solution. Only a nonsoluble fraction of molecules, above the solubility limit participates to the aggregation reaction. Above a certain concentration, this nonsoluble fraction is sufficiently large to form a gel with long fibres (very strong gel). At low concentrations, the length of the fibres may be weaker and the crystallites smaller giving the melting temperature more dependent on the concentration.

Rheological results

The curves of the elastic modulus G' and the loss modulus G'' versus time obtained during the time sweep experiments described before are represented in the Figure 4. This figure shows also the temperature T profile during the experiments (thick line). The comparison of the elastic modulus G' and the temperature T profiles shows that the gelation occurs during cooling as it has been visually observed. This behaviour does not allow observing the gelation phenomenon by the intersection of the loss factor $\tan\delta$ versus time curves measured isothermally at different frequencies. Indeed, the blends gel above the measurement temperature (*30°C*). It is found that G' is about ten times larger than G'' ($\tan\delta = G''/G' \approx 0.1$) as observed by others [6,13-15], confirming that the blends are gels.

Although the gelation occurs at temperatures higher than the measurement temperature, it is observed that the moduli continue to increase after gelation. So, it is necessary to wait a certain time t_r before G' reaches a constant value (rubbery plateau). Times t_r are reported in Table 1 and plotted versus concentration c in Figure 5. For concentrations greater than *2.5 wt%*, the time t_r is the same whatever the concentration and equal to that observed to reach the measurement temperature during cooling ($t_r \approx 20$ *min*). At concentrations lower than *2.5 wt%*, t_r increases when c decreases. It is interesting to note the similarity between the behaviours of T_{peak} and t_r (low variation above *2.5 wt%* and sharp variation below $c = 2.5$ *wt%*).

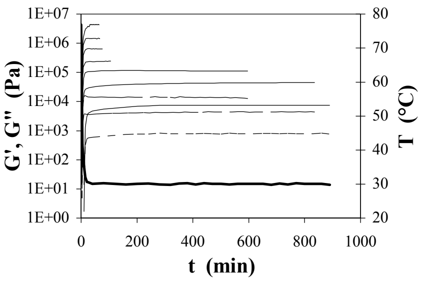


Figure 4. Elastic modulus *G'* and loss modulus *G''*(dotted line) of HSA/DGEBA blends versus time. From bottom to top *1.00, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00 wt%*

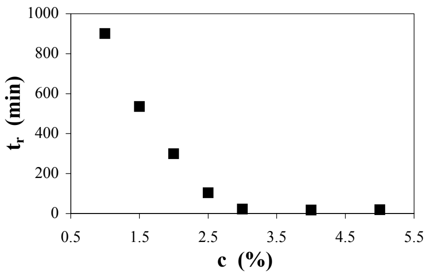


Figure 5. Time to reach the rubbery plateau HSA/DGEBA blends versus concentration

From the frequency sweep experiment performed when the rubbery plateau is reached, the curves of the elastic modulus *G'* and the loss modulus *G''* versus the angular frequency *ω* are represented in Figures 6 and 7.

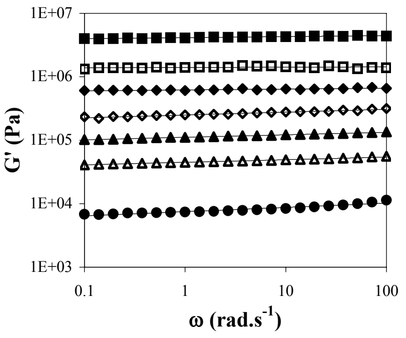


Figure 6. Elastic modulus of HSA/DGEBA gels versus angular frequency. From bottom to top *1.00, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00 wt%*

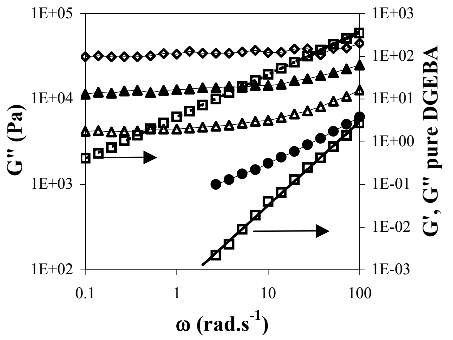


Figure 7. Loss modulus of HSA/DGEBA gels versus angular frequency. From bottom to top *1.00, 1.50, 2.00, 2.50 wt%*

Figure 6 shows that the curves *G'(ω)* are well fitted by the equation ($G' \propto \omega^{\Delta}$) represented by the lines on the curves. The values of exponent *Δ* have been reported in Table 1. These are small (*0.005* to *0.07*) and of the same magnitude as the one found by Terech et al [6] (*Δ* = *0.06* for HSA/dodecane gel at *4 wt%*). The very weak value of *Δ* indicates that *G'* is practically independent on the frequency within the domain considered as already observed [6,13-15]. This confirms once more that the materials tested are gels. Although *Δ* remains close to zero, it can be observed a significant increase in its values when the concentration becomes smaller than *2.5 wt%*. This change at *2.5 wt%* must be put in parallel with those observed for T_{peak} and t_r.

Figure 7 shows that the loss modulus *G''* is larger than the elastic modulus *G'* for pure DGEBA (secondary axis). Moreover, *G'* and *G''* are fitted respectively by the equations $G' \propto \omega^{1.96}$ and $G'' \propto \omega^{0.99}$ represented by the lines on the curves. These behaviours show that the pure DGEBA may be considered as a Newtonian liquid according to equations $G' \propto \omega^2$ and $G'' \propto \omega$.

If G' can be considered as constant for all concentrations over the entire range of frequencies, the behaviour of G'' is quite different (see Figure 7, primary axis). For concentrations higher than *2.5 wt%*, G'' is quite independent on the frequency. Below *2.5 wt%*, G'' depends on the frequency in the higher part of the frequency spectrum (for example at $c = 1$ *wt%*, $G'' \propto \omega^{0.50}$ for $\omega > 2$ *rad.s*$^{-1}$).

For a given frequency, it has been stated throughout the literature [6,14,21,22] that the elastic modulus follows a scaling law with concentration c ($G' \propto c^{\beta_1}$) or the distance from the critical concentration c^* ($G' \propto (c - c^*)^{\beta_2}$). Figures 8 and 9 respectively show the plot of *log* G' versus *log c* and the plot of *log* G' versus *log (c – c*)* with $c^* = 0.3$ *wt%* at angular frequencies *0.1, 1, 10 and 100 rad.s*$^{-1}$. For a better understanding, the curves have been shifted with a shift factor A reported on the figures. These curves have linear shapes, showing that both equations are verified. (Nevertheless, the fiting is better considering concentration c perhaps because of the uncertainty in the determinination of c^* which is visual). This is an indication that the gels have the same structure (perhaps rectangular cross-sectional shape of the fibres) whatever the concentration. This assertion is not in contradiction with the behaviour observed for T_{peak}, t_r and Δ as G' is a property of the gel phase. The values of β_1 and β_2 are listed in Table 3. β_1 and β_2 show a little decrease when the frequency increases. This is due to the fact that G' is more and more sensitive to the high frequency spectrum when the concentration decreases.

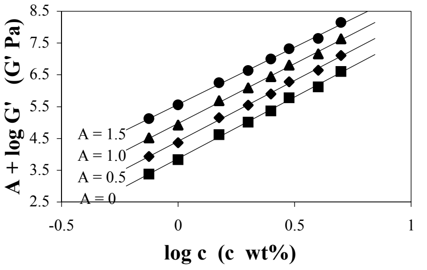


Figure 8. Logarithm of the elastic modulus of HSA/DGEBA gels versus logarithm of the concentration. From buttom to top 0.1, 1, 10, 100 Rad.s^{-1}.

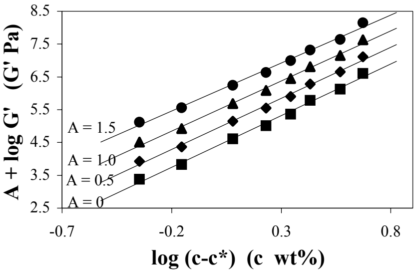


Figure 9. Logarithm of the elastic modulus of HSA/DGEBA gels versus logarithm of the distance from the critical concentration.

Table 3. Scaling exponents of (HSA/DGEBA) physical gels.

ω (*rad.s*$^{-1}$)	β_1	β_2
0.1	3.87	3.29
1	3.83	3.25
10	3.78	3.21
100	3.60	3.05

The curves of G' versus strain γ obtained from the strain sweep experiment are represented in Figure 10. These curves exhibit a linear domain up to a limiting value γ_l. The values adopted for strain in time sweep and frequency sweep experiments are in the linear domain. The linear domain is not large, especially at high concentrations, which indicates that the gels are fragile and can break easily. The values of γ_l have been reported in Table 2 and represented in Figure 11. It is observed that γ_l sharply increases when c decreases for concentration below *2.5 wt%.*

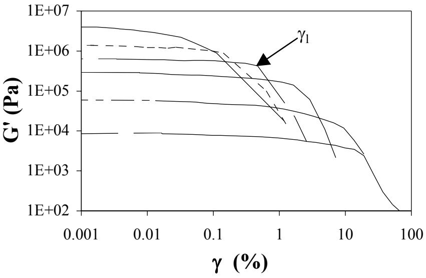


Figure 10. Elastic modulus (HSA/DGEBA) gels versus strain. From top to bottom *5.00, 4.00, 3.00, 2.50, 1.5 0, 1.00 wt%*

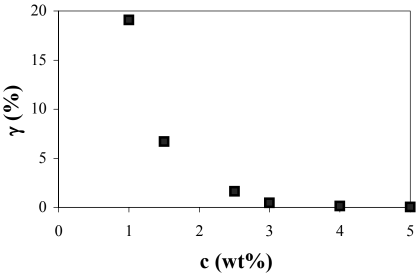


Figure 11. Limits of the linear domain on $G'(\gamma)$ curves HSA/DGEBA gels versus concentration.

Conclusion

Physical gels (organogels) formed of blend of 12-hydroxystearic acid (HSA) with two types of diglycidyl ether of bisphenol A (DGEBA) prepolymer with low degree of polymerization DGEBA ($n = 0.015$) were studied by differential scanning calorimetry (DSC) and dynamic rheology.

For concentration higher than $c^* = 0.3$ *wt%*, the mixture prepared at *80°C* form a reversible gel under cooling. According with the literature, the turbidity of the material indicates gels formed of fibres with rectangular cross-sectional shapes.

The enthalpy of melting of the blends exhibit a linear shape versus concentration with a slope $-183.7\ J.g^{-1}$ equal to the enthalpy of melting of the pure HSA ($-182 \pm 4\ J.g^{-1}$).

In the rubbery plateau, the elastic modulus G' is about ten times larger than the loss modulus G'' and G' is practically constant over the entire range of the frequency spectrum at a given concentration. These features show that the blends are gels.

From DSC experiments, the temperature T_{peak} of the endothermic peak was measured. Rheological experiments give:

- The time t_r to reach the rubbery plateau in time sweep experiments;
- The exponent Δ in the relation $G' \propto \omega^{\Delta}$ from frequency sweep experiments;
- The value γ_l limiting the linear domain in the strain sweep experiments.

The behaviours of T_{peak}, t_r, Δ and γ_l with the concentration are similar, i.e. sharp variation below *2.5 wt%* and light or no variation above *2.5 wt%*. The sharp variation below *2.5 wt%* is attributed to smaller crystallites in the blend. The behaviour of G'' is consistent with this observation, as it is sensitive to the higher part of the frequency spectrum at low concentration.

The elastic modulus follows a scaling law with concentration. The scaling exponent is *3.87 ± .02* at *1 rad.s*$^{-1}$. The scaling law indicates that the structure of the gel is the same whatever the concentration.

Acknowledgements. The authors acknowledge Institut de Recherche Scientifique pour le Développement en Coopération, Aire Développement and Ministère Français de la Coopération for financial support.

References

[1] Terech P., and Weiss R. G. (1997) Chem. Rev. 97:3133.
[2] Tachibana T. and Kambara H. (1972) Bull. Chem. Soc. Jap. 42:336.
[3] Taniguchi Y. and Suzuki K. (1974) J. Phys. Chem. 78:759
[4] Terech P. (1992) J. Phys. France 2:2181.
[5] Terech P., Rodriguez V., Barnes J. D., and McKenna G. B. (1994) Langmuir 10:3406.
[6] Terech P., Pasquier D., Bordas V., and Rossat C. (2000) Langmuir 16:4485.
[7] Tamura T., Ichikawa M. (1997) JOACS 74:491.
[8] Tamura T., Suetake T., Ohkubo T., and Ohbu K. (1994) JOACS 71:857.
[9] Tachibana T. and Kambara H. J. (1968) Colloid Interface 28:173.
[10] Tachibana T., Yoshizumi T., and Hori K. (1979) Bull. Chem. Soc. Jap. 52:34.
[11] Tachibana T., Mori T., and Hori K. (1980) Bull. Chem. Soc. Jap.53:1714.
[12] Tachibana T., Mori T., and Hori K. (1981) Bull. Chem. Soc. Jap. 54:73.
[13] Fabri D., Guan J., Cesaro A. (1998) Thermochimica Acta 321:3.
[14] Piau J-M., Dorget M., and Palierne J-F. (1999) J. Rheol. 43:305.
[15] Mercurio D. J., Khan S. A., Spontak R. (2001) J. Rheol. Acta 40:30.
[16] Liu X. Y. and Sawant P. D. (2001) Appl. Phys. Let. 79:3518.
[17] Girard-Reydet E., and Pascault J. P. (2000) (2000) Macromolecules 33:3084.
[18] Eloundou J. P., Ayina O., Noah Ngamveng J. (1998) Eur. Polym. J. 34:1331.
[19] Eloundou J. P., Fève M., Gérard J. F., Harran D., and Pascault J. P. (1996) Macromolecules 29:6907.
[20] Eloundou J. P., Gérard J. F., Harran D., and Pascault J. P. (1996) Macromolecules 29:6917.
[21] Lin Y.-C. and Weiss R. G. (1987) Macromolecules 20:414.
[22] Khan S. A., and Zoeller N. J. (1993) J. Rheol. 37:1225.
[23] Arauguren M. I., Mora E., De Groot J. V. Jr., and Macosko C. W. (1992) J. Rheol. 36:1165.