Viscoelastic Properties of Thermoreversible Gels from Chemically Modified PVCs†

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ABSTRACT: Two homologous series of polymers based on poly(vinyl chloride) (PVC) have been prepared by chemical reduction of PVC with lithium aluminum tetrahydride and by chemical substitution of PVC with sodium benzenethiolate. The general formula for both series of copolymers is $(CH_2CHCl)_m-(CH_2-CHX)_n$, with $X = H$ or SC_6H_5 for the first or second reaction, respectively, and n varying from 0 to 50% or more. The microstructure of both series of copolymers has been analyzed in terms of stereoregularity and chemical composition distribution by ^{13}C- and ^{1}H-NMR spectroscopy. It is found that, for a given copolymer composition in both series, the chain length is the same and Cl atoms from isotactic and atactic placements are preferentially eliminated. Gels of these two series of copolymers of different molar composition were prepared at several concentrations in a series of diester like solvents, varying the acid and alcohol size of the diester. The viscoelastic properties of these gels using parallel-plate shear and tensile compression modes were evaluated as a function of temperature. The storage moduli were analyzed using different new theories proposed for the elasticity of gels: those of Clark and Ross-Murphy and of Jones and Marques. These results provide evidence for an enthalpic origin of the elasticity of PVC gels. This interpretation is in agreement with the results obtained from small-angle neutron scattering for both series of gels in deuterated diethyl oxalate, in which a fiber-like structure for PVC gels is assumed.

Introduction

During the last few years, a range of new studies on polymer thermoreversible gels have emerged, on the one hand investigations in the field of analysis of molecular structure with the aid of small-angle neutron scattering (SANS) and quasi-elastic light scattering and, on the other, studies concerning the numerous applications of those materials in sensors and in controlled delivery systems for fungicides, powders, etc. The interest in these gels comes from the fact that a tridimensional network which provides an elastic character is formed.

One of the most widely studied thermoreversible gel behaviors is that of PVC, which has been found to form gels in numerous solvents. These studies have been devoted mainly to the viscoelastic properties and, more recently, to the analysis of the molecular structure of the gels.[1] In the last few years, new research has pointed toward the possibility that ordered structures other than syndiotactic sequences are also involved in the junctions. In this respect, Yang and Geil[2] established that crystallization in PVC/solvent gels is independent of the gel network formation. To these authors, gel-forming ability and gel hardness are functions of the polymer−solvent interaction and the H-bonding ability of the solvent. On the other hand, Huang et al.,[3] studying plasticized PVC by SAXS, observed an increase in the radius of gyration with increasing plasticizer content, which suggests an expansion of the domains, and pointed to the possibility that these domains may not be entirely crystalline. Nevertheless, there are still some important questions to be answered or demonstrated: What is the nature of the network? Is it formed by crystalline junctions, segment−segment association, or polymer−solvent association as has recently been proposed? What is the nature of the chlorine involved? What is the role of solvent in the gel formation? Is the gelification mechanism of PVC similar to that of other polymers? In an attempt to answer these questions, a European project has been undertaken between five laboratories, where different work has been programmed. The work reported here has been carried out under the framework of this project.

In the study of the gelification mechanism of PVC in several diesters, by means of DSC, viscoelastic properties, and SANS, it has been found by Guenet et al.[1,4−6] that the diester solvent molecules most probably participate in the formation of additional links, giving further support to a fibrilar model, proposed by the same authors in agreement with the fibrous network structure suggested by Yang and Geil.[2] In this model, it is assumed that, because of the polarizability of the C═O and the Cl−C−H bonds, each carbonyl group can interact with two different chains, thus helping to establish new junctions (weak links) responsible for the high values of elastic modulus.

In the study of the viscoelastic behavior of thermoreversible PVC gels in DOP, Santamaria et al.[7,8] applied the Clark and Ross-Murphy cascade model and analyzed the results under the hypothesis of a liquid−liquid phase separation model as being responsible for the relativy high values of the storage modulus.

In the initial study of PVC thermoreversible gels by means of chemically modified PVC,[9] we found that the storage modulus of gels based on thiobenzene-substituted PVC in dioctyl phthalate gradually decreases as a function of chlorine elimination, thus indicating that

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the gel formation is gradually inhibited. The gel formation in PVC was associated with normal chlorines from iso- and heterotactic placements. More recently,[10] the molecular structure of thermoreversible gels based on chemical modified PVC in deuterated diethyl oxalate has been investigated by small-angle neutron scattering. The results are analyzed considering noncompact polydispersed fibers, arising from the formation of a polymer−solvent complex, as is described in detail in ref 10.

To extend the knowledge of the viscoelastic properties of PVC gels in relation with polymer structure and solvent, a new study has been programmed in this work. It consists of the preparation of polymers based on PVC, the determination of viscoelastic properties of gels of these polymers in different solvents, and the interpretation of results as a function of new elasticity theories for thermoreversible gels.

Experimental Part

Materials. A commercial PVC sample prepared by block polymerization was kindly supplied by ATO CHEM Industries, Spain. The number-average molecular weight, determined by osmometric measurements, is $M_n = 32\,000$. The tacticity measured by ^{13}C-NMR spectroscopy is rr = 30.7, mr = 49.8, and mm = 19.6.

Lithium aluminum hydride ($LiAlH_4$) was purchased from Merck and used without further purification. Sodium benzenethiolate (NaBT) was synthesized from the reaction of sodium with thiophenol in *p*-xylene as previously described.[11,12]

Cyclohexanone (CH) was distilled twice prior to use. Tetrahydrofuran (THF) was also distilled.

Diethyl oxalate (DEO), dibutyl oxalate (DBO), diethyl succinate (DES), diethyl malonate (DEM), and dibutyl malonate (DBM), supplied by Merck, were used without further purification.

EPVC Copolymers. EPVC copolymers were obtained by the chemical reduction of PVC with $LiAlH_4$ in THF under conditions detailed by Pourahmady et al.[13] and López et al.[10] The chemical composition of EPVC copolymers $(CH_2-CHCl)-(CH_2CH_2)$ was determined by ^{1}H-NMR spectroscopy. In copolymers EPVC(*X*), *X* is the content of E units in mole % in the copolymer.

SPVC Copolymers. SPVC copolymers were obtained by the substitution reaction of PVC with NaBT in the melt in a Brabender plasticorder at 160 °C and 40 rpm according to a method previously described.[11] The chemical composition of SPVC copolymers $(CH_2CHCl)-(CH_2CHSC_6H_5)$ was determined by GPC as is detailed in refs 11 and 14. In copolymers SPVC(*X*), *X* is the content of VBT units in mole % in the copolymer.

Polymer Microstructure. The microstructure of the EPVC and SPVC series was analyzed by ^{13}C-NMR spectroscopy in 5% w/v solution in deuterated dioxane. The measurements were undertaken using a 300 MHz XL Varian spectrometer operating at 75.5 MHz and 90 °C, using conditions previously described.[15] The resonances used were those of methine carbons of the VC-centered triads ranging from 57 to 66 ppm.

The calculations were carried out by measuring the relative areas of the different peaks of the methine carbons with a compensating polar planimeter.

Gels. Homogeneous gels of 20% w/w were prepared by dissolving the corresponding sample from the EPVC or SPVC series in DEO, DBO, DES, or DEM at 160 °C under conditions of vigorous stirring until the polymer was completely dissolved. Solutions were poured onto drying plates and cooled to room temperature for 24 h. Homogeneous gels of PVC, EPVC, and SPVC in DEO and DBO were also prepared at concentrations ranging from 12 to 30% w/w.

Viscoelastic Measurements. Dynamic viscoelastic measurements were performed on a Carri-Med CSL 100 rheometer using the parallel-plate shear mode to measure the storage modulus, G', the loss modulus, G'', and the loss tangent, tan δ. To avoid the influence of aging on the G' modulus, measurements for all of the samples were performed 24 h after the gels were prepared, under the following conditions: temperature sweep from 30 to 150 °C; plate diameter, 2 cm; frequency, 1 Hz; temperature scan, 4 °C/min; torque, 20 μN·m; and displacement, 5×10^{-4} rad. The linear viscoelastic region was located with the aid of a torque sweep.

Dynamic viscoelastic measurements were also performed on gels about 1 cm high on a Metravib viscoelasticimeter, Mod Mark 03, using the tensile compression mode, to measure Young's modulus E'. The continuous heating was in the range 30−120 °C at a frequency of 5 Hz.

Results and Discussion

As discussed in the Introduction, there are many studies concerning viscoelastic behavior of PVC gels. In most of them, the formtion of the tridimensional network responsible for the high modulus was attributed to physical junctions established in the crystalline zone of the chain, although it has been demonstrated that crystallinity, which arises from syndiotactic sequences, cannot be the only factor to explain such high values of modulus. These structural aspects of PVC continue to be a subject of research in numerous laboratories. Nevertheless, there are no systematic analyses regarding either the polymer microstructure or the amount and nature of the Cl atoms involved in the gel behavior of PVC. It is obvious that any attempts to reproduce PVC microstructure from chlorinated PE, or to obtain highly crystalline PVC from polymerization, result in failure. Another attempt involved varying the number of Cl atoms by the chlorination of PVC, but in this case the radical character of this reaction also made it difficult to obtain a controllable structure.[16]

We think that a useful approach to the study of the influence of PVC microstructure in the gel behavior of the polymer is to correlate homologous series of PVC prepared from the same polymer chain by controlled modification reactions, with the elastic properties and molecular structure of gels prepared from them. Of course, these homologous series must fulfil a series of requirements, as will be shown in the next section.

Polymers Based on PVC. As was previously reported,[10,15] chemical reaction on PVC is an easy way to prepare PVC structures of the general formula $(CH_2\text{-}CHCl)-(CH_2CHX)$, which can be considered as a homologous series of PVC with variable number of Cl atoms, with the same chain length and well-characterized vinyl chloride microstructure. Two methods described in the Experimental Section have been employed in this work: reduction reactions to obtain the EPVC series, where X = H, and substitution reactions to obtain the SPVC series, where $X = SC_6H_5$.

In Figures 1 and 2, the ^{13}C-NMR spectra for EPVC and SPVC copolymers with various chlorine contents are shown. Compositional and configurational triad assignments are reported for the spectra. From these spectra, the content of mm, mr, and rr VC triads can be calculated for each copolymer according to the methods described in refs 13 and 15. In Figure 3, the content of isotactic, heterotactic, and syndiotactic chlorines are plotted for different molar compositions of the two series of copolymers. From this figure, it can be seen that, whether by substitution or reduction reactions in the PVC chain, Cl atoms are preferentially replaced from isotactic or heterotactic placements and that, for the same copolymer composition, the isotactic, heterotactic, and syndiotactic Cl content does not change from SPVC to EPVC.

From the ^{13}C-NMR spectra of the EPVC series and ^{1}H-NMR spectra of the SPVC series published else-

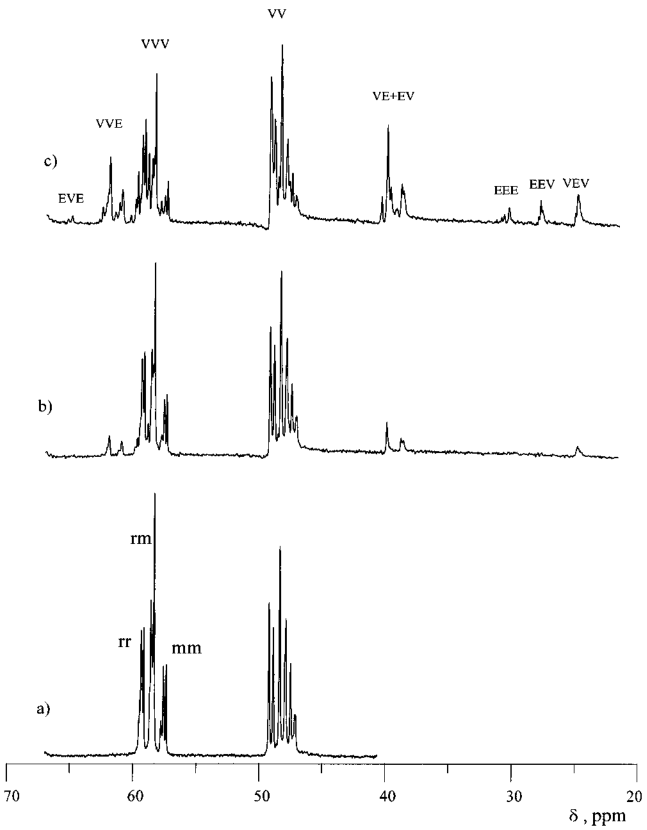

Figure 1. ^{13}C-NMR spectra of (a) PVC, (b) EPVC(5), and (c) EPVC(17).

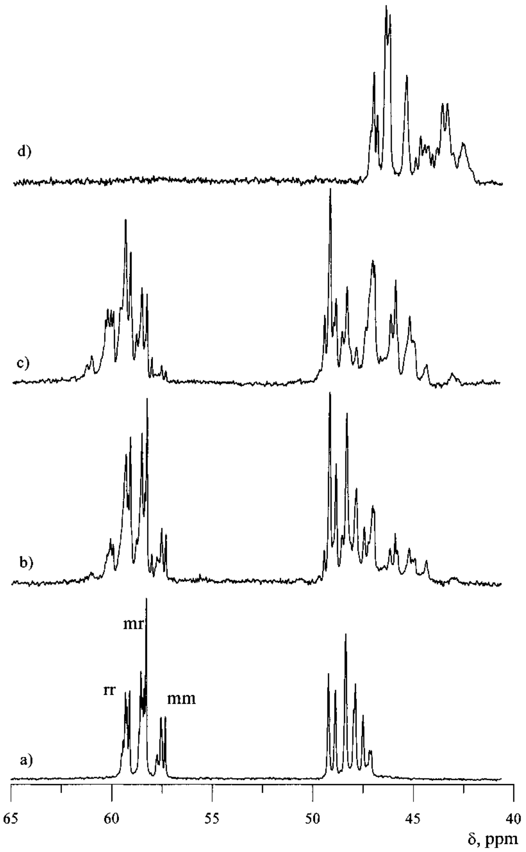

Figure 2. ^{13}C-NMR spectra of (a) PVC, (b) SPVC(10), (c) SPVC(30), and (d) SPVC(100).

where,[13,15,18] it is possible to calculate the VVV, VVE, EVE, VEV, VEE, and EEE compositional triads for the EPVC copolymers and the VVV, VVS, SVS, VSV, VSS, and SSS compositional triads for the SPVC copolymers, respectively. The evolution of the different compositional triads with molar composition corresponds to a random substitution for the two series. These results are in agreement with those found by calorimetric measurements of both series of copolymers, which give T_g values that also correspond to those calculated for random copolymers.[18] As reported elsewhere,[17,18] in these reactions there are no side reactions, such as scission or cross-linking. As a consequence, the molecular size (chain length) for all copolymers (and for both series) is the same as that of the original PVC.

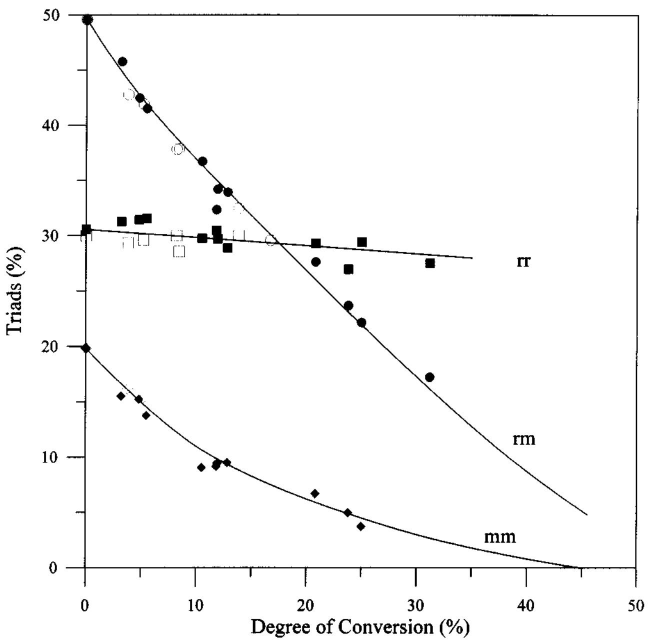

Figure 3. Evolution of mm, mr, and rr triads with degree of Cl elimination in EPVC (solid symbols), and SPVC (open symbols).

Therefore, both copolymers, $(CH_2CHCl)_m-(CH_2CHX)_n$ with $X = H$ or SC_6H_5, can be considered as homologous series of PVC in which m can vary from 100 to 0. If n is small, the behavior of any copolymer of the series can be representative of the PVC behavior in which n Cl atoms are randomly eliminated from the PVC chain. Of course, the possible influence of the X group must also be considered in the results.

Viscoelastic Properties. Several authors[2,6,7,19] have studied the influence of different parameters, such as molecular weight, crystallinity, concentration, aging, and temperature, on the storage modulii of PVC gels. More recently, it has been demonstrated that the solvent plays an essential role in the formation of the networks.[1] But not studies on underchlorinated PVC can be found in the literature. For this reason, our purpose is to study the evolution of viscoelastic properties of PVC gels as functions of the content and nature of chlorine, temperature, and concentration in order to apply different theories of gel elasticity and to look deeper into the gelation mechanism of PVC. For that reason, all other parameters or preparation conditions are maintained the same for all the samples.

As an example, Figure 4 plots the evolution of the storage modulus with temperature for various SPVC gels, with variable Cl content, in DEO. The same behavior as that observed for gels of these polymers in dioctyl phthalate is found.[9] That is, chlorine elimination from the polymer gradually decreases the storage modulus, thus indicating that the network formation

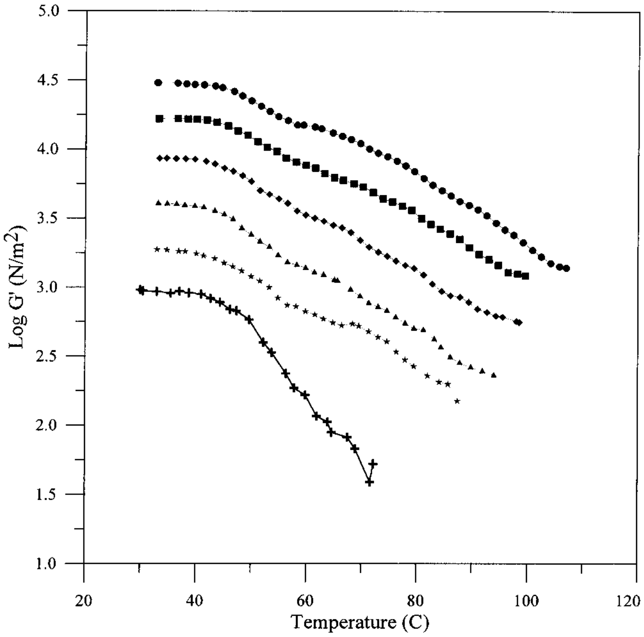

Figure 4. Evolution of storage modulus, *G*, of SPVC gels in DEO with temperature as a function of chlorine substitution (top to bottom): (●) 0.0%, (■) 1.6%, (◆) 3.2%, (▲) 5.3%, (★) 6.8%, and (+) 10.0%.

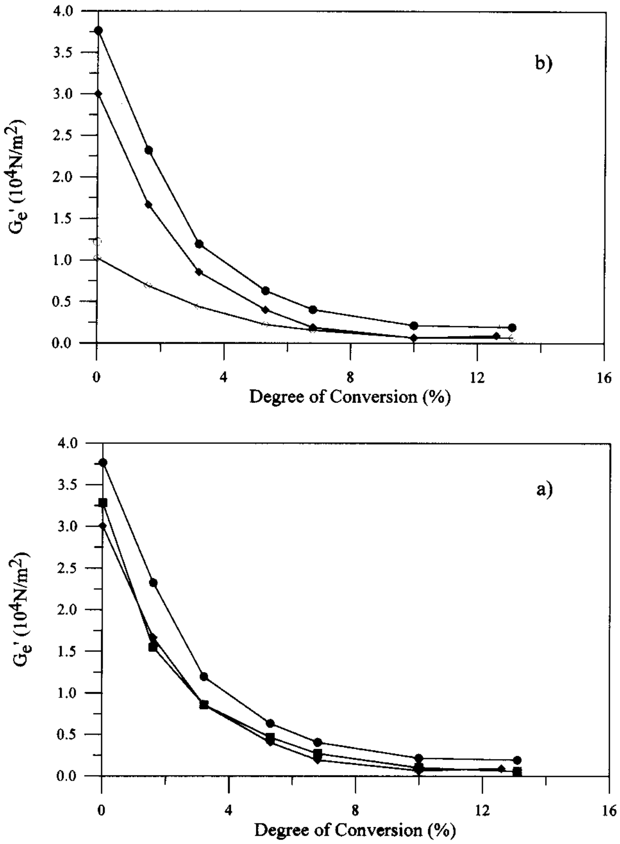

Figure 5. Storage modulus taken at $T = 30$ °C, G_e', versus chlorine elimination of SPVC gels prepared (a) in DEM (●), DES (■), and DEO (◆) and (b) in DEM (●) and DBM (○) and in DEO (◆) and DBO (◇).

is inhibited in a parallel way. Gels prepared from SPVC(15), or those with lower Cl content, do not form macroscopic gels. Similar results are obtained for gels of these polymers in all of the solvents studied.

To determine the effect of the solvent and that of the polymer in the viscoelastic properties of PVC gels, gels have been prepared from the two series of polymers described above in a series of diester solvents with different acid and alcohol size. The storage modulus of gels from EPVC and SPVC with variable Cl content in the diester solvents as a function of the temperature has been measured. To analyze the effect of alcohol size, DEO and DBO on the one hand, and DEM and DBM on the other, were chosen. To study the effect of acid size, the same kinds of gels in DEM, DEO, and DES were prepared.

From plots like those in Figure 4, we can define a temperature-independent plateau modulus G_e': we take G_e' as the value of the storage modulus at $T = 30$ °C. In Figure 5, the evolution of storage modulus, G_e', as a function of the eliminated chlorine, expressed in mole %, for gels of SPVC in a series of diester solvents is plotted. The effect of acid size of the diester on G_e' of gels prepared in DEO, DEM, and DES is analyzed in Figure 5a; that of the alcohol size in DEO and DBO and in DEM and DBM is given in Figure 5b. In both figures, it can be observed that (1) as chlorine is gradually suppressed, the storage modulus decreases gradually for all of the diesters studied; (2) as the size of the acid increases in the diester, the storage modulus of SPVC at any Cl content remains similar; and (3) as the size of the alcohol increases in the diester from ethyl to butyl, the storage modulus decreases.

These results can be interpreted with the aid of the Guenet's model in the following way. In the model, each carbonyl of the diester can interact with two different chains, giving rise to the development of aggregates by means of the formation of a bridge, and thus generating gels of high elastic moduli. If Cl atoms from iso- and heterotactic placements are gradually suppressed, the formation of polymer–solvent–polymer bridges will be inhibited, and therefore the modulus will decrease progressively. This explanation and the Guenet's model are confirmed separately[20] by the study, by ^{1}H-NMR spectroscopy, of the correlation of polymer–diester interactions in gels of PVC and chemically modified PVC in DEO and DBO with their elastic properties and molecular structure. In this work, a large polymer–solvent interaction, which is gradually suppressed either by temperature or by chlorine elimination, is shown. On the other hand, the degree of interaction is greater in DEO than in DBO.

The effect of polymer structure in the viscoelastic properties of the gels is shown in Figure 6, where the variation of the storage modulus, G_e', of gels from EPVC and SPVC in DEO with chlorine elimination, in mole %, is plotted. By comparing gels from the EPVC and SPVC, it is observed that, for any Cl content, the storage modulus of EPVC gels is higher than that of SPVC gels. Following the results of the study of the molecular structure of these gels by small-angle neutron scattering (SANS), this phenomenon can be interpreted mainly as being due to the fact that H substitution suppresses the bond polarization, while benzene substitution does not necessarily preclude the bond polarization required for polymer–solvent interaction. However, the interaction between DEO and this group seems to be so strong that swelling occurs, which eventually decreases the network density. It can be added that a steric effect from the SC_6H_5 group can also limit the approach of the solvent in order to establish the junctions.

Molecular Interpretation. Our viscoelastic results, and in particular the concentration dependence of G_e', have been analyzed using two different theoretical approaches: the cascade model of Clark and Ross-

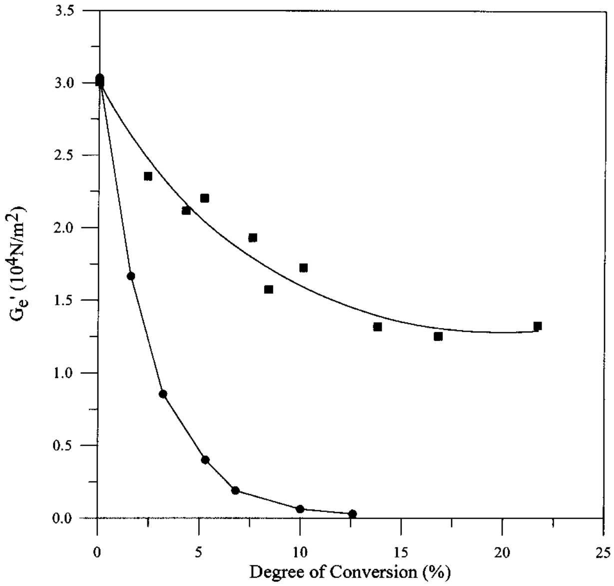

Figure 6. Comparison of storage modulus, G_e', as a function of chlorine elimination (■) EPVC gels and (●) SPVC gels in DEO.

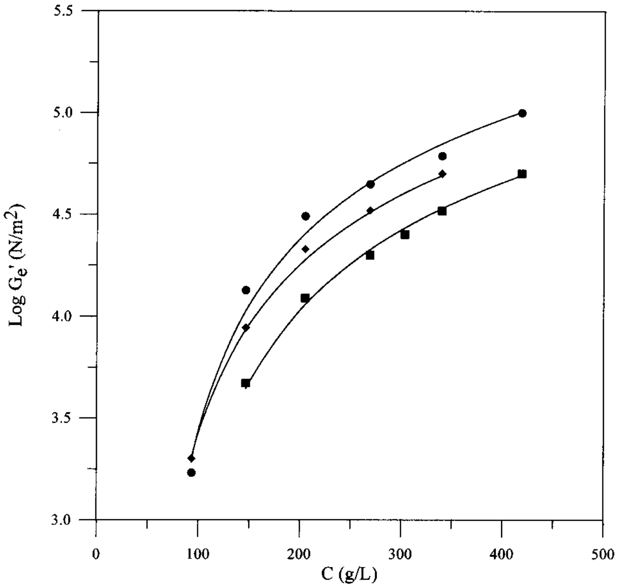

Figure 7. Log of the storage modulus, G_e', versus polymer concentration, ϕ, for gels of (●) PVC, (◆) EPVC(1.7), and (■) SPVC(1.6) in DEO. The full curves correspond to the best fit applying the cascade model.

Murphy[21–23] and the rigid network model of Jones and Marques.[24] Our aim is not to establish which one describes better the viscoelastic behavior (in fact, both models describe well our results), nor to discuss whether the formed objects are fractals, but to correlate the interpretation of the trends observed experimentally with the basic parameters of both theories.

In the cascade model, the elastic modulus is factorized in two terms, one describing the number of elastically effective chains and the other the contribution per chain to the modulus. The latter includes the chain stiffness effect. The basic parameters of this model are the molecular weight of the gel-forming polymer, *M*, the number of sites available for bonding to others, *f*, the equilibrium constant, *K*, for the making and breaking of bonds, and the generalized front factor, *a*. The front factor *a* allows the contribution *aRT* to the elastic modulus, rather than *RT* as in the classical (entropic) theory of rubber elasticity. This theory has been applied with success to a number of thermoreversible gels, although the values found for the functionality *f* to obtain good modulus–concentration fits are, in some cases, difficult to justify.

According to this model, the number of elastically active network chains per primary chain is given by

$$N_1 = [f\alpha(1 - \nu)^2(1 - \beta)]/2 \qquad (1)$$

where *f* is the functionality (number of sites per polymer chain potentially available for bonding to others), α is the proportion of functionalities that have reacted, ν is the extinction probability, obtained from

$$f - 1 = \ln \nu/\ln(1 - \alpha + \alpha\nu) \qquad (2)$$

and β is

$$\beta = (f - 1)\alpha\nu/[1 - \alpha + \alpha\nu] \qquad (3)$$

The critical concentration, in weight percent, just able to form a gel is given by

$$c_0 = M(f - 1)/[1 - Kf(f - 2)^2] \qquad (4)$$

where *M* is the molecular weight and *K* an equilibrium constant given by

$$K = \alpha/Nf(1 - \alpha)^2 \qquad (5)$$

where *N* is the number of moles of polymer per liter.

The equation that gives *G* (in Pascals) is

$$G_e = \frac{aRT(f - 1)\alpha(1 - \nu)^2(1 - \beta)}{2K(f - 2)^2}\frac{c}{c_0} \times 1000 \qquad (6)$$

where the front factor *a* is a parameter measuring the deviation from ideal rubber elasticity: $a > 1$ signifies that there are enthalpic contributions to the elastic modulus.

To apply the Cascade model, we must fix the functionality *f* and optimize the values of *a* and *K*. As has been pointed out in previous work,[7] we can assume that the network of PVC gels originates from small crystals (serving as physical cross-links) of approximately 40 Å, which for a crystallinity of 8% and molecular weight M_n = 32 000 gives rise to $f = 3$. In the case of the modified PVCs (SPVC and EPVC), syndiotactic sequences (which play the most important role in crystallization) do not change with degree of substitution (see Figure 3). This leads us to assume that the functionality to be use in the cascade model is the same for PVC-, SPVC-, and EPVC-based gels. In Figure 7, the log–log plots of G_e' against concentration for gels of PVC, EPVC(1.7), and SPVC(1.6) in DEO are shown, as an example, together with the corresponding best fits obtained applying the Cascade model. In Tables 1 and 2, the optimized values for the parameters *a* and *K* used in eq 6 for all polymers of the SPVC and EPVC series in DEO and DBO, respectively, are summarized. We can observe that *a*, the parameter that accounts for the enthalpic contribution to elastic modulus, tends to 1 as the degree of substitution increases. We can also see that the lower values of *a* correspond to the gels of SPVC, which indicates that the enthalpic contribution to the elasticity decreases as the capacity to form weak links diminishes.

The effect of the solvent on the elasticity of the gels is also explained on the basis of the polymer–solvent interactions. As can be seen in Figure 5b, gels prepared

Table 1. Optimized Values for the Parameters *a* and *K* Used in Eq 6 with $f = 3$[a]

sample	conversion (%)	*K* (L/mol)	*a*
PVC	0.0	413	6.5
SPVC1	1.4	373	3.5
SPVC2	3.2	279	2.5
SPVC3	5.3	246	1.5
SPVC4	10.0	160	1.5
EPVC1	1.7	473	7.7
EPVC2	3.8	291	7.5
EPVC3	6.3	380	7.0
EPVC4	8.9	296	5.5
EPVC5	11.1	396	6.5

[a] Gels in DEO.

Table 2. Optimized Values for the Parameters *a* and *K* Used in Eq 6 with $f = 3$[a]

sample	conversion (%)	*K* (L/mol)	*a*
PVC	0.0	352	2.5
SPVC1	1.4	285	2.5
SPVC2	3.2	262	1.5
SPVC5	6.8	262	1.5
SPVC4	10.0	150	1.5
EPVC2	3.8	219	6.5
EPVC4	8.9	221	4.5
EPVC5	11.1	250	7.5

[a] Gels in DBO.

using DBO present lower elastic moduli than those prepared by DEO. We attribute this result to the fact that shorter (fewer carbon atoms) alcohol in DEO expedites the formation of weak links, which give rise to an elasticity of enthalpic origin, i.e., the existence of rigid, fiber-like structures. The variation of the parameter *a* from the cascade model, shown in Tables 1 and 2, is compatible with this interpretation, since lower values of this parameter are found for gels prepared using the larger (more carbon atoms) DBO solvent, which hinders the formation of weak links.

On the other hand, Jones and Marques pattern rigid networks as stiff elements joined at cross-linking points: the elasticity will depend on the stiffness of the elements, as well as on the degree of mobility of the chains at each cross-link point. Therefore, the enthalpic and entropic types of elastic behavior can be simultaneously present, depending on the rigidity of the chains and on the magnitude of the fluctuations of the angle between two chains about an average value. Besides the reasons invoked when applying the cascade model to our experimental data (consider the meaning of $a > 1$), there are two reasons to assume that enthalpic contribution to the modulus is important. One is because, in the evolution of the shear modulus, *G*, as a function of the temperature, a plateau independent of the temperature is observed between 30 and 50 °C for all the gels. This behavior is usually found in gels of enthalpic origin. The second reason comes from the results of a parallel study of molecular structure of the same gels by SANS.[10] In that work, we have measured the molecular density of gels from EPVC and SPVC polymers in DEO, one of solvents studied in this work. In that study, the fiber-like gel structure model receives additional support, i.e., rodlike structure, in which enthapic elasticity is predominant. It is shown[10] that a small modification in the PVC chain significantly alters the gel structure, although different results have been found for the two series. In the EPVC series, the molecular density decreases (but not dramatically) between PVC and EPVC(10) samples (the change is about 18%), but in SPVC polymers the substitution involves larger effects than for H substitution. This may stem from the fact that the chemical group is far larger than a chlorine atom, thus leading to steric effects, but also this type of substitution improves the polymer–solvent interaction, which thereby produces a swelling effect (going from rodlike to Gaussian).

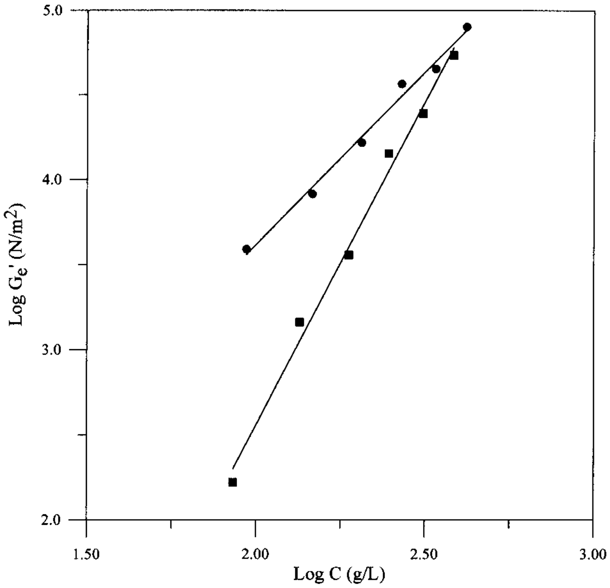

Figure 8. Log–log plot of storage modulus, G_e', versus polymer concentration for gels of PVC prepared in DEO (●) and DBO (■).

The model of Jones and Marques leads to the following equation for the elastic modulus *G*:

$$G = G_r G_e/(G_e + G_r) \tag{7}$$

where G_r and G_e represent the enthalpic and entropic contributions, respectively.

G_r is obtained considering that the network may only deform by bending, which leads to the following scaling with concentration ϕ:

$$G_r \propto \phi^{(3\epsilon+1)/(3\epsilon-1)} \tag{8}$$

where ϵ is the inverse of the fractal dimension.

G_e is determined assuming that chains are freely hinged in the sense that, if we isolate from the network the chains meeting at a cross-link point, there will be no constraint on the angles between the chains. The elasticity of this entropic network of rigid chains scales with concentration:

$$G_e \propto \phi^{3\epsilon/(3\epsilon-1)} \tag{9}$$

As an example, the double-logarithmic plot of G' versus ϕ for PVC gels in DEO and DBO is plotted in Figure 8. In this figure, it is noticed that the larger gradients are found for gels prepared using DBO as a solvent. Actually, from eqs 8 and 9, we can deduce that, the higher the gradient of log G'–log ϕ, the lower is ϵ, and the larger the fractal dimension, $1/\epsilon$, is. For a network of rodlike chains, the fractal dimension would be 1, such that we can confirm that the increase of the fractal dimension of gels based on DBO, with respect to DEO, indicate to us that the chains are more flexible in the former system.

Although not shown here, similar plots were obtained for gels of copolymers of the EPVC and SPVC series in DEO and DBO from which the fractal dimensions are

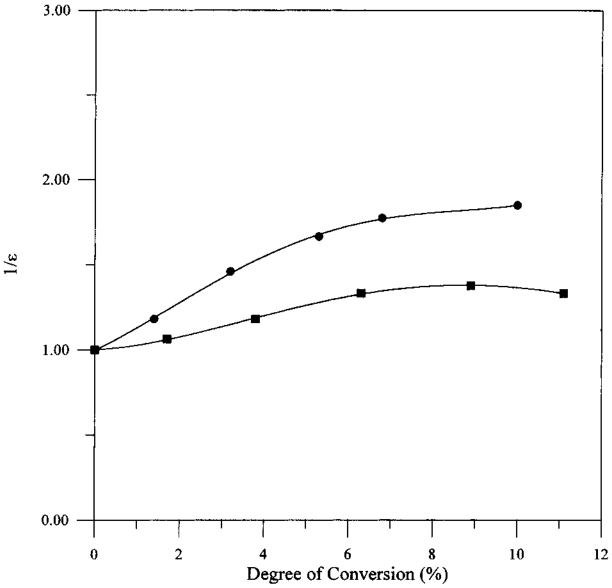

Figure 9. Fractal dimension, 1/ϵ, versus Cl elimination for gels of the series SPVC (●) and EPVC (■) in DEO.

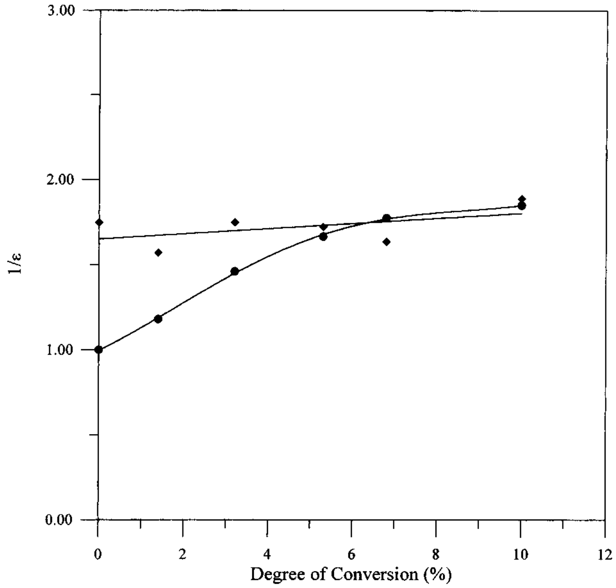

Figure 10. Fractal dimension, 1/ϵ, versus Cl elimination for gels of the series SPVC prepared in DEO (●) and DBO (◆).

determined. In Figure 9, the fractal dimension, 1/ϵ, versus chlorine elimination for gels of EPVC and SPVC in DEO is plotted. Accordingly, the enthalpic contribution is lessened and the elasticity tends to become entropic, a result also envisaged from the analysis of the front factor *a* of the Cascade model, as shown in Tables 1 and 2. We consider this an effect of the progressive inability of formation of a polymer−solvent complex, which would account for the fiber-like structure, as the number of substituted PVC chain chlorines is decreased. This polymer−solvent complex is said to occur through weak links that, as has been observed by neutron scattering,[10] gradually dissappear with increasing degree of modification of PVC. The fiber rigidity is therefore lessened in SPVC- and EPVC-based gels, whose elasticity becomes less enthalpic as the presence of a flexible, as opposed to rigid, structure is increased. It is also worth pointing out the differences found in the elastic moduli of gels from SPVC and EPVC: in Figure 7, it can be seen that EPVC gives rise to more elastic gels (higher *G*′) for the same degree of substitution. This can be explained as a consequence of the difficulties that the benzenethiolate group poses to the solvent to reach the chain, such that few weak links can be formed as compared to the much less bulky hydrogen atoms of the EPVCs, which do not hinder the polymer−solvent bridge.

In Figure 10, the fractal dimensions of the SPVC series in DEO and DBO are compared. As can be observed, in gels prepared in DBO, higher fractal dimensions are found than in those prepared in DEO, and the change with conversion is not so pronounced. A study of molecular structure of gels in DBO by SANS has been programmed in order to confirm the results.

Conclusions

By reduction and substitution reactions on PVC, two series of PVC copolymers have been obtained in which the content of syndiotactic chlorine and the chain length in all copolymers of both series are similar to those of the original PVC. The eliminated Cl in both series belongs to the less stereoregular parts, i.e., to isotactic and heterotactic configurations.

The modulus of the gels of the polymers of the two series in a range of diesters gradually decreases as the number of chlorine atoms decreases. The difference is larger for thiobenzene-substituted PVC than for reduced PVC.

The analysis of the dependence of elastic modulus with polymer concentration for all the polymers in diethyl oxalate, using the cascade model and a model for rigid networks, shows an enthalpic origin for the elasticity of PVC gels. This elasticity behavior changes from enthalpic to entropic, i.e., less rigid structures, as the chlorine atoms are eliminated. On the other hand, this finding is consistent with a rigid structure, which has also been obtained in the analysis of the molecular structure of these gels by small-angle neutron scattering, where the molecular structure can be modeled by a fiber-like structure assuming PVC−solvent weak links. These junctions take place through interactions betwen carbonyls of the diester and H−C−Cl, as is demonstrated by ^{1}H-NMR spectroscopy in a separate work,[20] thus confirming the fibrillar model proposed by Guenet for the gelification of poly(vinyl chloride).

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