Study of Poly(vinyl chloride) Gels by Means of Stereospecific Substitution Reactions

C. Mijangos* and D. López

CSIC, Instituto de Ciencia y Technología de Polímeros, Juan de la Cierva 3, Madrid 28006, Spain

M. E. Muñoz and A. Santamaría

Departamento de Ciencia y Tecnología de Polímeros, Facultad de Químicas, UPV/EHU, Barrio Ibaeta s.n. San Sebastian, Basque Country, Spain

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ABSTRACT: Poly(vinyl chloride) (PVC) has been chemically modified with sodium benzenethiolate in the melt, i.e., in the absence of solvent, and in cyclohexanone, a solvent favoring polymer interactions. Viscoelastic measurements of gels based on PVC substituted samples in the melt as a function of the degree of chlorine elimination show that the storage modulus gradually decreases, thus indicating that gel formation is gradually inhibited. The results from polymers modified in cyclohexanone follow the same behavior as those modified in the melt, but the storage modulus values are higher. In the latter case the possibility of additional links in the polymer is suggested. ^{13}C-NMR spectroscopy demonstrates that only central chlorines of heterotactic and isotactic triads are eliminated; thus, either one or both types of chlorine must be associated with gel formation in poly(vinyl chloride).

Introduction

Since the early work of Alfrey et al.[1] poly(vinyl chloride) (PVC) has been known to exhibit a strong tendency to form associated structures in solution, which manifest themselves macroscopically by gelation. In recent years, this problem has become very topical, and several authors have focused their attention on the very nature of the chlorine implicated in the formation of gels in solvents such as dioctyl phthalate,[2-6] diethyl malonate, other esters,[7-14] and ketones.[15-20] Nevertheless, the gelation mechanism and the nature of the physical links have still not been elucidated, although different explanations have been proposed, including crystallites, intermolecular hydrogen bonding, and phase separation into polymer-rich and polymer-poor regions.

Viscoelastic Properties of PVC. Research on the rheology of gels has been focused on the variation of the modulus (obtained by compression, shear, or elongation under steady or dynamic conditions) with concentration and gel fusion temperature studies. In this sense, the main contribution of dynamic viscoelastic measurements has been to determine accurately a temperature- and frequency-independent modulus to relate it to the nature of tie points which give rise to the gel. Although reports on dynamic viscoelastic measurements of PVC-based gels are few, Santamaría et al.[2,3] have examined the dynamic storage modulus and the loss tangent of this type of gel, detecting the existence of two pseudoequilibrium moduli independent of temperature, frequency, and strain amplitude. These results have been interpreted as a symptom of the participation of another type of link, besides crystallites, in the formation of the structure of aged gels. In addition, it was observed that this behavior was consistent with liquid–liquid phase separation.[3] By calorimetric studies, Guenet et al.[9,20] have shown the existence of a second endotherm at lower temperatures, perfectly reproducible in spite of its low value. They thought it to arise from the ordering of the less stereoregular sections.

Reactions of PVC. The possibility of demonstrating the nature of the links in PVC gels by chemical reactions has already been reported by Dorrestijn et al.[4] They studied the storage modulus of PVC and postchlorinated PVC and found that a 13% molar concentration of additional chlorines introduced by random chlorination in solution completely supresses gelation, in contrast with the bulk chlorinated samples. The differences found were ascribed to the influence of the intramolecular chlorine distribution on crystallizability.

Stereoselective substitution reactions on PVC allow the controlled elimination of the PVC chain chlorines, and the nature of the eliminated chlorines can be identified by ^{13}C-NMR. Thus, we have reported that the reaction of PVC with sodium benzenethiolate in the melt, either in a continuous or in a discontinuous process,[21,22] in cyclohexanone solution,[23] and in aqueous suspensions[24] always takes place through the central chlorines of isotactic and heterotactic triads.

Furthermore, the study of the glass transition temperature of modified PVC with the same reactant in different solvents and media such as cyclohexanone, tetrahydrofuran, and dioxane as well as in the melt has shown that for the same chemical composition the corresponding T_g of the polymer depends on the nature of the solvent for the reaction.[25]

In this study, the effect of the controlled substitution of PVC chain chlorines on the gelation properties is examined. To determine the nature of the eliminated chlorines, the stereostructural evolution has been carried out by ^{13}C-NMR. Viscoelastic measurements of modified polymers in the melt and in cyclohexanone solutions are also reported.

Experimental Section

Materials. The PVC sample was a commercial polymer prepared by block polymerization furnished by Rio Rodano Industries, Spain. The number-average molecular weight, determined by osmometric measurements, is M_n 32000, and the tacticity, measured by ^{13}C-NMR, is s = 30.7, h = 49.8, and i = 19.6.

Sodium benzenethiolate was synthesized from the reaction of sodium with thiophenol as described in earlier articles.[23,24] Cyclohexanone was distilled twice prior to use. Tetrahydrofuran and bis(2-ethylhexyl) phthalate (DOP) were also distilled.

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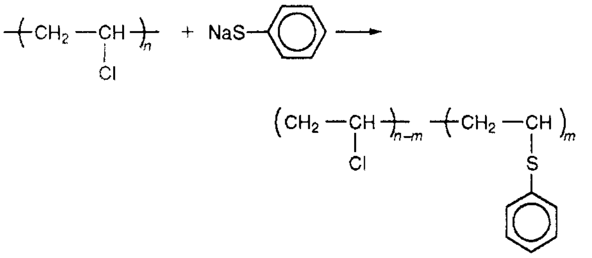
Substitution Reactions. The substitution reactions of PVC with benzenethiolate in the melt using DOP as a plasticizer and stearic acid as a lubricant were performed in a Brabender Plasticorder system (reaction 1). The reactions were carried out in a single step for different quantities of polymer, nucleophile, and plasticizer. The processing conditions were 160 °C and 40 rpm. At appropriate reaction times samples were drawn out, purified three times with THF–MeOH as the solvent–precipitant system, and dried at 40 °C under vacuum for 2 days. The chemical composition of the samples was determined by UV spectroscopy by a method described elsewhere.[23]



(1)

The substitution reaction of PVC with benzenethiolate in cyclohexanone was carried out at 60 °C. To obtain the required conversions, the reactions were performed in a single step for different reaction mixtures and, at appropriate times, samples were withdrawn, precipitated immediately with methanol, and then purified and analyzed as previously described.

Characterization of Polymers. The number-average molecular weights of the samples were obtained by osmometric measurements carried out at 34 °C with solutions in cyclohexanone using a Knauer membrane osmometer.

The stereochemical structures of both the initial and modified polymers were studied by means of ^{13}C-NMR spectra obtained from solutions in deuterated dioxane on a 300-MHz XL Varian spectrometer operating at 75.5 MHz and 90 °C using conditions described previously.[21–23,26]. The resonances used were those of the methine carbons of the backbone, ranging from 57.0 to 60.0 ppm, which give the relative proportions of isotactic, heterotactic, and syndiotactic triads. The calculations were carried out by measuring the relative areas of the different peaks of the methine carbons with a compensating polar planimeter.

Gel Preparation. Homogeneous gels with 20% (w/w) PVC were prepared by the following procedure: The polymer was dissolved in DOP at 160 °C with vigorous stirring until the polymer was completely dissolved. The solutions were then poured into drying plates and cooled to room temperature for 24 h. Solutions prepared at 160 °C or higher temperatures have no influence on the values of the moduli G' and G''.[3] Solutions prepared from polymers whose degree of conversion is >10% for polymers modified in the melt, and 12% for polymers modified in solution do not give consistent gels.

To make suitable comparisons between copolymers with different degrees of benzenethiol incorporated into the chain and the same amount of free benzenethiol, gels from PVC–thiophenol mixtures were prepared using the same conditions as above.

Viscoelastic Measurements. Dynamic viscoelastic measurements were performed on a Carri-Med CSL100 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,[3–6] the measurements for all the samples were performed 24 h after the gels were prepared. The operating conditions were the following: temperature sweep between 30 and 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. Frequency scans in isothermal conditions were also carried out.

Results and Discussion

Structural Evolution of PVC with Degree of Substitution. Molecular Weight Evolution with Degree of Substitution.

The effect of molecular weight on the mechanical and rheological properties of PVC gels is a function of the type of solvent. For instance, it has been reported by Mutin et al.[9] that for gels prepared in bromonaphthalene there is a twofold increase of compression modulus when the molecular weight is doubled, while for gels prepared in diethyl malonate there is no variation. For PVC gels prepared in dimethyl phthalate, dioxane, and other solvents, Geil et al.[15] have shown that variation in the molecular weight of the PVC has a strong effect upon the gel melting temperature of the polymer. At the same time, it has also been reported that the processing of virgin PVC under high temperature and shear leads to the degradation and thus to the scission and/or crosslinking of the polymer. Consequently, we have to verify whether any minor side degradation reactions have taken place during the substitution of polymer with sodium benzenethiolate in the melt.

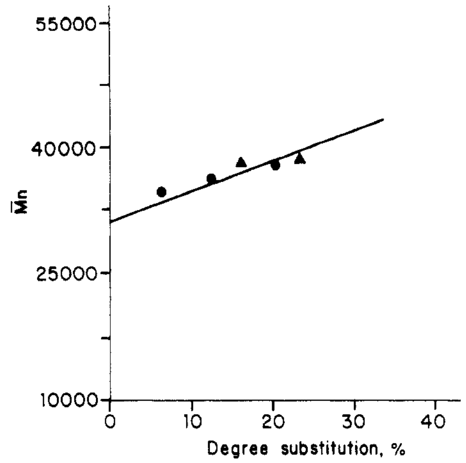


Figure 1. Evolution of the number-average molecular weight with degree of chlorine substitution: (●) melt; (▲) cyclohexanone; (—) theoretical.

Figure 1 shows the number-average molecular weight of the substituted PVC as a function of degree of substitution for the melt and cyclohexanone reactions, together with the theoretical evolution of M_n with conversion. In this figure it can be seen that the experimental M_n values follow the calculated evolution, and thus there is no indication of any scission or cross-linking in the modified polymer in either the melt or solution. Consequently, the molecular weight cannot be responsible for any decrease in the variation of elastic modulus with degree of substitution or for the difference in the moduli between the melt and cyclohexanone substituted PVC gels.

Stereostructural Evolution with Degree of Substitution. The microstructure of PVC modified by sodium benzenethiolate with degree of conversion has been characterized by ^{13}C-NMR spectroscopy. Figure 2, represents the evolution of the unreacted chlorines of isotactic, heterotactic, and syndiotactic triads with degree of substitution. The data in Figure 2 are from the published literature[26–30] and this work. It can be observed in both the melt and cyclohexanone reactions that only chlorines in heterotactic and isotactic configurations are eliminated, the heterotactic chlorines decreasing in intensity more rapidly. Syndiotactic triads increase only apparently due to the formation of new β-substituted syndiotactic triads. In fact, by Monte Carlo simulation of the reaction kinetics and that of the evolution of the polymer microstructure, a value of almost zero has been found for the reactivity of the syndiotactic triads.[26,29]

Dynamic Viscoelasticity of Modified PVC Gels. In Figure 3 we present the storage modulus (G') and loss

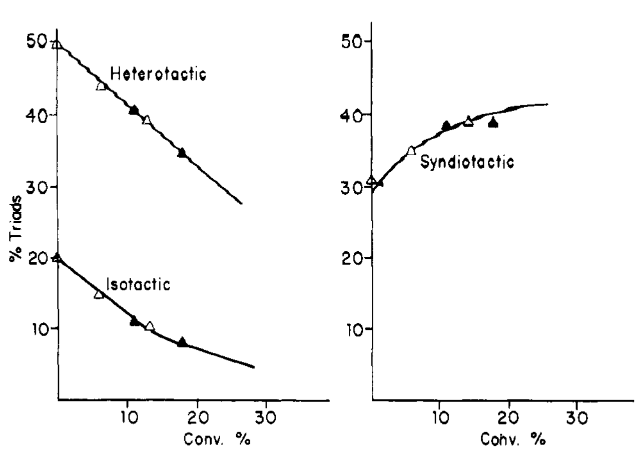


Figure 2. Evolution of chlorine content with degree of substitution of isotactic, heterotactic, and syndiotactic triads: (△) melt; (▲) cyclohexanone; (—) results of published works.[26-30]

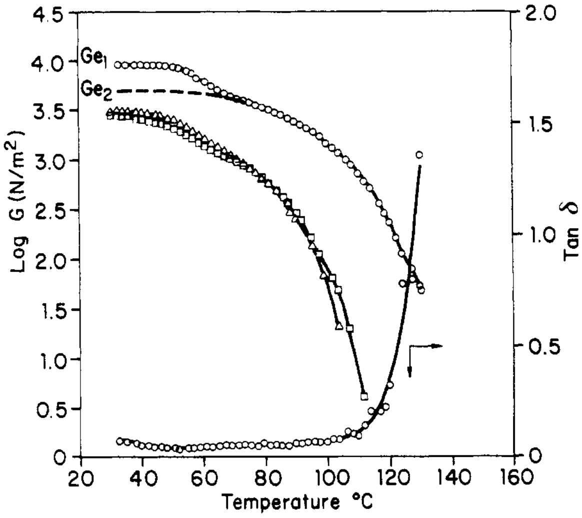


Figure 3. Storage modulus (G) and loss tangent (tan δ) versus temperature for gels from (○) virgin PVC, (△) 5.5% substituted PVC in cyclohexanone; (□) 5.25% substituted PVC in the melt.

tangent (tan δ) taken at a frequency of 1 Hz as a function of temperature for the virgin PVC gel as well as various modified (melt and solution) PVC gels. Taking into account our previous results,[2,3] the spectra can be considered as typical of PVC aged gels, allowing us to define the following parameters: G'_e = the storage modulus at the first plateau (low temperatures); T_s = the temperature at which transition from the first plateau to the second plateau takes place, its value being obtained from the minimum of the first derivative; and T_f = the temperature of fusion, defined as the temperature for which tan $\delta = 1$ according to the criterion discussed in ref 2. Even though in a previous paper[3] it has been suggested that the lower plateau G'_{e_2} corresponds to the system gelled by crystallization and that the plateau G'_{e_1} corresponds to gelation in the polymer-rich region, which includes the possibility of another type of link, the results are also consistent with the interpretation given by Mutin and Guenet[9,14] about the existence of ordered structures which may be due to the participation of the solvent in the formation of gel junctions.

Although no accurate definition is available to describe physical gels, in terms of mechanical properties it has been said that a gel should be characterized by an elastic modulus at zero frequency. Therefore, the existence of gels in substituted PVC–DOP systems can be inferred from the frequency scans presented in Figure 4. The parameters defined above, which characterize the viscoelastic behavior of PVC and modified PVC gels, are presented in Table I.

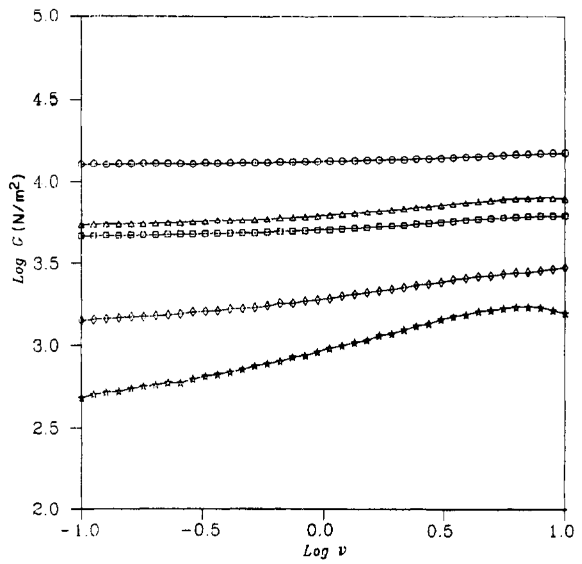


Figure 4. Storage modulus versus frequency at T = 30 °C as a function of degree of substitution: (○) 0; (△) 1.2; (□) 3.2; (◇) 5.3; (☆) 6.8%.

Table I. Viscoelastic Parameters of Substituted PVC

sample	medium	conv (%)	$10^{-3}G'_{e_1}$ (N/m^2)	$10^{-3}G'_{e_2}$ (N/m^2)	T_f (°C)	T_s (°C)
1		0.0	9.3	4.9	128	63.3
2		10.0[a]	7.0	5.1		56.3
3		20.0[a]	4.4	3.4		55.2
4	melt	0.0[b]	8.8	6.6	130	59.6
5	melt	1.2	8.0	5.5	125	58.5
6	melt	3.2	5.7	3.6	114	58.4
7	melt	5.3	4.4	2.3	106	61.2
8	melt	6.8	2.9	1.5	96	58.0
9	melt	10.0		0.6	57	
10	melt	13.0				
11	CH	0.0[c]	12.1	8.1	132	60.9
12	CH	1.7	9.6	6.1	121	55.9
13	CH	2.7	7.2	4.4	116	61.7
14	CH	4.5	6.5	3.2	99	56.7
15	CH	6.5	6.2	3.0	95	61.0
16	CH	7.3	4.2	1.6	90	57.8
17	CH	10.0		1.3	68	
18	CH	16.0				

[a] Refers to the mole percentage of free thiol in the PVC–thiophenol mixture. [b] PVC processed in the melt under the reaction conditions without reagent. [c] PVC treated in the cyclohexanone under the reaction conditions without reagent.

Effect of Degree of Substitution for Modified PVC in the Melt. Figure 5 shows the temperature dependence of the storage modulus as a function of degree of chlorine substitution. From this figure and that corresponding to tan δ, the values of G'_{e_1}, G'_{e_2}, T_f, and T_s are obtained, and they are given in Table I. To compare the data of gels based on modified PVC in the melt, an analysis of the evolution of G'_{e_1}, G'_{e_2}, and T_f with degree of substitution is presented in Figure 6. In this figure the following features can be observed as the amount of substituted chlorine increases: (i) Both G'_{e_1} and G'_{e_2} decrease sharply, (*ii*) the difference between G'_{e_1} and G'_{e_2} decreases, (iii) the melting temperature T_f decreases, and (iv) for 10% substitution a gel cannot be obtained.

The result of applying a substitution reaction to the polymer using sodium benzenethiolate brings about both the elimination of Cl atoms and its replacement by benzenethiol groups (see reaction 1). If we apply the Mutin and Guenet model,[9-14] we can explain the above results easily by the following arguments.

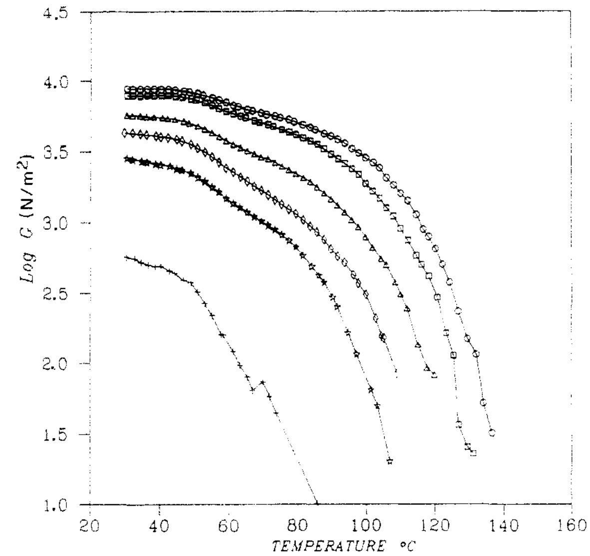


Figure 5. Storage modulus versus temperature as a function of the degree of chlorine substitution at 1 Hz: (○) 0; (□) 1.2; (△) 3.2; (◇) 5.3; (☆) 6.8; (+) 10.0%.

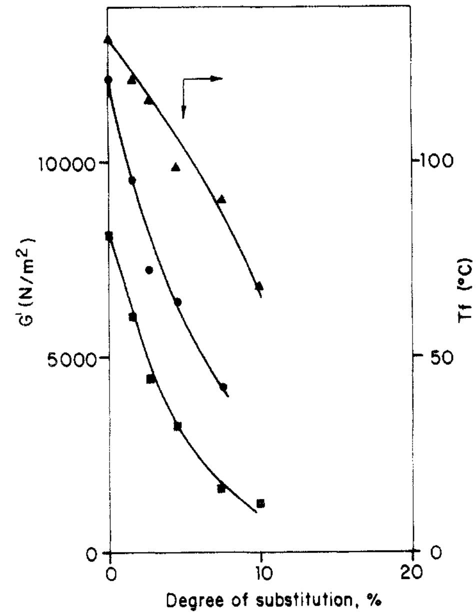


Figure 6. Plot of (●) G'_{e_1}, (■) G'_{e_2}, and (▲) T_f as a function of degree of substitution of PVC modified in the melt.

Firstly, Mutin and Guenet assume that in the case of diesters each carbonyl group can interact with two different chains, giving rise to the aggregates by the formation of two bridges (see description in ref 9) and thus to a gel of high G' modulus. Now, if we gradually eliminate the Cl atoms from the PVC chain, the formation of polymer–solvent–polymer bridges will be inhibited and the G' modulus will decrease. In addition, the benzenethiol group grafted on the PVC chain may sterically hinder the diester's access to the chain, leading also to the attenuation of bridge formation, contributing again to the decrease in G' modulus.

Second, to support the above explanation and thus Guenet's model, we have initiated the same kind of studies with reduced PVC where Cl are replaced by H atoms. In this case the steric hindrance with the diester will not be important, and gel formation will not be easily prevented. Although this work is not yet finished, preliminary results are that, for the same Cl content, the reduced PVC form DOP gels of higher G' values than benzenethiolate substituted PVC, as expected.

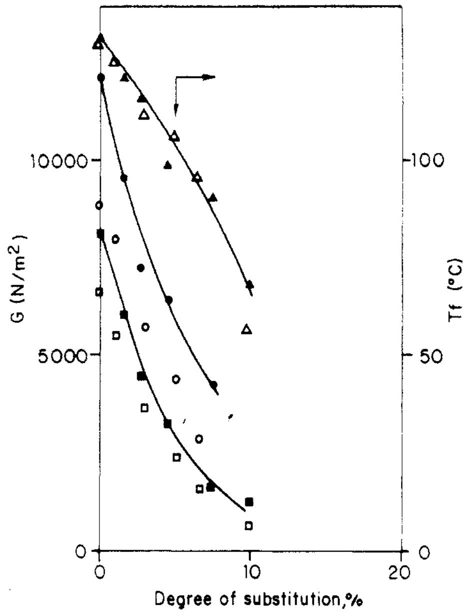


Figure 7. Plot of (●) G'_{e_1}, (■) G'_{e_2} and (▲) T_f of PVC modified in cyclohexanone. Open points correspond to PVC modified in the melt.

Third, according to the hypothesis of Guenet et al.,[9-14] it is expected that free benzenethiol mixed with PVC and DOP would have only a diluent effect in the formation of gel. Thus gels formed from these mixtures should have high G' values, attenuated only by a concentration effect. In Table I, runs 2 and 3 correspond to values of G' of two experiments with free benzenethiol. It should be noted that the values of the storage modulus are proportional to the PVC concentration.

From these results we conclude that we can associate the gradual decrease in the storage modulus with the controlled elimination of chlorine and therefore with the decrease in Cl of heterotactic and/or isotactic triads, as has been demonstrated by previous NMR results[26-30] and this work. Further, about a 10% chlorine substitution clearly suppresses gel formation in PVC.

Although these results seem to be unusual, previous studies on PVC gels pointed out that structures other than syndiotactic are involved in the formation of PVC gels.[1-20]

Effect of Degree of Substitution on PVC in Solution. Gels of PVC modified with sodium benzenethiolate in a cyclohexanone solution give the same features as those obtained for the melt modified polymers. The results are compared in Figure 7. G'_e. G'_{e_2}, and T_f all decrease with degree of chlorine elimination, and no gels are formed above a conversion of 12%. Nevertheless, the values of G'_{e_1} and G'_{e_2} for the same chemical composition are higher for the polymer modified in cyclohexanone.

Although the interpretation of the differences observed above is not simple, these results are in good agreement with those found in the study of the glass transition temperature for the same polymers.[25] The polymer modified in cyclohexanone had a higher T_g than the polymer modified in the melt for the same degree of substitution. The difference was interpreted in terms of polymer–polymer interactions. That is, in the PVC modified in cyclohexanone there exist at local sites on the chain some interactions which are either self-associations (Coleman et al.[31]) or new interactions produced by the cyclohexanone (Maddams et al.[17,18]) which prevent chain mobility and are thus responsible for the high T_g. This hindered mobility of the samples gives rise to a packing effect, which could be the cause of the higher moduli observed in Figure 7.

The above results do not seem to be in agreement with those of Dorrestijn et al.[4] For us, bulk substitution (melt) is certainly random, since the substituted polymers follow the Fox equation in the evolution of T_g with chemical composition.[25] The polymer substituted in cyclohexanone follows the same microstructure evolution as that of the melt (refs 21–30 and results of this work). We believe that the distribution of the substitution cannot be responsible for the difference in the storage moduli. However, the formation of gels from PVC substituted in the cyclohexanone and melt should take place through the same type of chlorines. ^{13}C-NMR studies at the pentad level of these samples is now under way and will allow us to determine more accurately the length of the structure involved in gel formation. On the other hand, additional links of cyclohexanone substituted polymers could give rise to networks of different size.

The purpose of this work was neither to elucidate the role of polymer–solvent interactions nor to clarify the molecular arrangement in the gel but rather to show that, by using a controlled substitution reaction on PVC, it is possible to carry out a novel study of the mechanism of gel formation in poly(vinyl chloride). Studies now in progress on elastic and quasielastic light scattering will allow us to correlate the aggregate size with the number and the nature of chlorines implied in the formation of PVC gels.

Conclusions

We can conclude that, by applying a stereospecific substitution reaction on PVC, it is possible to gradually eliminate the formation of gels in poly(vinyl chloride). Since stereospecific substitution reactions eliminate chlorines from isotactic and heterotactic triads, gel formation must be associated with isotactic or heterotactic sequences of the polymer. The reactions carried out in carbonyl solvents presumably lead to additional links in the polymer and hence to a higher storage modulus than in the case where the solvent is absent (the melt).

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References and Notes

(1) Alfrey, T.; Wiederhorn, N., Jr.; Stein, R.; Tobolsky, A. *J. Colloid Sci.* **1949**, *4*, 221.
(2) Gallego, F.; Muñoz, M. E.; Peña, J. J.; Santamaría, A. *J. Polym. Sci.* **1988**, *26*, 1871.
(3) García, A. I.; Muñoz, M. E.; Peña, J. J.; Santamaría, A. *Macromolecules* **1990**, *23*, 5251.
(4) Dorrestijn, A.; Lemstra, P. J.; Berghmans, H. *Polym. Commun.* **1983**, *24*, 226.
(5) Dorrestijn, A.; te Nijenhuis, K. *Colloid Polym. Sci.* **1990**, *268*, 895.
(6) te Nijenhuis, K.; Winter, H. H. *Macromolecules* **1989**, *22*, 411.
(7) Najeh, M.; Munch, J. P.; Guenet, J. M. *Macromolecules* **1992**, *25*, 7018.
(8) Abied, H.; Brûlet, A.; Guenet, J. M. *Colloid Polym. Sci.* **1990**, *268*, 403–413.
(9) Mutin, P. H.; Guenet, J. M. *Macromolecules* **1989**, *22*, 843.
(10) Klein, M.; Guenet, J. M. *Macromolecules* **1989**, *22*, 3716.
(11) Mutin, P. H.; Guenet, J. M.; Hirsch, E.; Candau, S. J. *Polymer* **1988**, *29*, 30.
(12) Mutin, P. H.; Guenet, J. M. *Polymer* **1986**, *27*, 1098.
(13) Candau, S. J.; Dormoy, Y.; Mutin, P. H.; Deveauvais, F.; Guenet, J. M. *Polymer* **1987**, *28*, 1334.
(14) Guenet, J. M. *Thermoreversible Gelation of Polymers and Biopolymers*; Academic Press: New York, 1992.
(15) Yang, Y. C.; Geil, P. H. *J. Macromol. Sci., Phys.* **1983**, *B22*, 463.
(16) Bowley, H. J.; Gerrard, D. L.; Maddams, W. F. *Polym. Commun.* **1986**, *27*, 43.
(17) Jackson, R. S.; Bower, D. O.; Maddams, W. F. *Polymer* **1990**, *31*, 857.
(18) Jackson, R. S.; Bower, D. I.; Maddams, W. F. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 837.
(19) Bower, D. I.; Jackson, R. S. *J Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1589.
(20) Chalykh, A. Ye; Sapozhnikova, I. N.; Bulgakova, R. A.; Sokolova, N. P. *Polym. Bull.* **1988**, *19*, 501.
(21) Mijangos, C.; Gómez-Elvira, J. M.; Martínez, G.; Millán, J. *J. Appl. Polym. Sci.* **1989**, *38*, 1685.
(22) Mijangos, C.; Cassagnau, P.; Michel, A. *J. Appl. Polym. Sci.* **1992**, *44*, 2019.
(23) Millán, J.; Martínez, G.; Mijangos, C. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1077.
(24) Martínez, G.; Terroba, P.; Mijangos, C.; Millán, J. *J. Polym. Sci. Polym., Chem. Ed.* **1988**, *26*, 1629.
(25) López, D.; Mijangos, C. *Colloid Polym. Sci.*, in press.
(26) Spitz, R.; Llauro-Darricades, M. F.; Michel, A.; Guyot, A.; Mijangos, C.; Martínez, G.; Millán, J. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1753.
(27) Mijangos, C.; Martínez, G.; Millán, J. *Eur. Polym. J.* **1986**, *22* (5), 423.
(28) Millán, J.; Martínez, G.; Mijangos, C.; Mendez, A.; Gómez-Elvira, J. M.; Gómez Daza, M. *Makromol. Chem., Macromol. Symp.* **1988**, *20/21*, 49.
(29) Spitz, R.; Llauro-Darricades, M. F.; Michel, A.; Guyot, A.; Mijangos, C.; Martínez, G.; Millán, J. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *20*, 99.
(30) Millán, J.; Martínez, G.; Jimeno, M. L. *Eur. Polym. J.* **1991**, *27* (6), 483.
(31) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing Co. Inc.: Lancaster, PA, 1990.