

Physical Gels from Poly(vinyl chloride): Effect of Solvent Type

Mohamed Najeh, Jean-Pierre Munch, and Jean-Michel Guenet*

Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes,[†]
 Université Louis Pasteur-CNRS URA 851, 4, rue Blaise Pascal,
 67070 Strasbourg Cedex, France

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ABSTRACT: The gelation of poly(vinyl chloride) has been studied in homologous diesters and monoesters. The relation between the modulus, E , and the swelling degree, G_v , at swelling equilibrium has been found to depend upon the solvent type. Two classes of universality have been found obeying power laws: gels in monoesters, $E = 24.5G_v^{-2.72 \pm 0.1}$ kPa; gels in diesters, $E = 18.6G_v^{-1.54 \pm 0.1}$ kPa. Light scattering investigations on aggregates have also revealed two types of behavior depending upon whether diesters or monoesters are used. Finally, DSC experiments show that diester solvent molecules most probably participate in the formation of additional links (polymer-solvent complexes) while monoester solvent molecules act essentially as plasticizers. The experiments reported herein give further support to a model first suggested by Mutin and Guenet.

Introduction

The gelation capability of atactic poly(vinyl chloride) (PVC) has been known for over 40 years,¹⁻³ and yet the gelation mechanism is still not thoroughly elucidated. While there now seems little doubt that some crystallization is involved in the physical junctions formation, it is difficult to reconcile the low degree of crystallinity that can reach atactic PVC (usually less than 10%) with the high elastic moduli achievable. As was recently pointed out by He et al.,⁴ PVC gels possess compression moduli as large as those measured for thermoreversible gels prepared from multiblock copolymers containing 50% of crystallizable (and actually crystallized) sequences. Clearly, there must be some additional links or some additional phenomenon, the origin of which needs to be elucidated.

The possibility for the existence of ordered structures other than those formed by the syndiotactic sequences of the PVC chains has already been evoked by Juijn et al.⁵ These authors consider that sequences containing a few isotactic defects can still be incorporated into the crystalline lattice with a minimum distortion of the latter. Recently, Mutin and Guenet⁶ and Abied et al.⁷ have suggested that the solvent may participate in the formation of this second type of gel junction. They assume in the case of diesters that, thanks to 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.

The purpose of this paper is to test Mutin and Guenet's suggestion by comparing the compression moduli of gels formed with diesters, for which the above process is feasible, with gels prepared from monoesters for which no additional links can be formed that way. To be conclusive, this study has been achieved at comparable swelling and swelling equilibrium. Also, light scattering experiments carried out on aggregates formed in dilute solutions of either diesters or monoesters will be reported and discussed together with the mechanical properties of the corresponding gels. Finally, calorimetry investigations will provide further support to the molecular models deduced from this study.

Experimental Section

(1) **Materials.** The PVC sample provided by Rhovyl S.A. was already used in previous studies.^{6,7} It is mainly atactic, as

* To whom correspondence should be addressed.

[†] Formerly Laboratoire de Spectrométrie et d'Imagerie Ultrasonores.

ascertained by the determination of the triad content by a ¹³C NMR from a clear 10% solution in cyclohexanone (syndio = 0.33, iso = 0.18, and hetero = 0.49). Its molecular weight characteristics as determined by GPC in THF are⁶ $M_w = 1.2 \times 10^5$ with $M_w/M_n \approx 2.3$.

Three types of solvent were used in this study: ethyl monoesters [$\text{CH}_3(\text{CH}_2)_n\text{CO}_2\text{C}_2\text{H}_5$], with $n = 2-8$; isoamyl acetate [$(\text{CH}_3)_2\text{CHCO}_2(\text{C}_4\text{H}_9)$]; diethyl esters [$(\text{CH}_2)_n(\text{CO}_2\text{C}_2\text{H}_5)_2$], with $n = 0-10$; dibutyl esters [$(\text{CH}_2)_n(\text{CO}_2\text{C}_4\text{H}_9)_2$], with $n = 0, 2, 4, 6$.

All the solvents were of high purity grade and were used without further purification. Their names together with their chemical formulas, abbreviations, and molar volumes are listed in Table I.

(2) **Sample Preparation.** In order to achieve precise determination of the compression modulus, samples must possess a cylindrical shape, with a height being approximately the same as the diameter. In addition the faces of the cylinder must be as parallel as possible. We previously prepared such samples by cutting the ends of a gel that had been formed in a test tube beforehand.⁶ Here we have used another method which allows one to obtain gels possessing highly parallel faces. To achieve highly parallel faces in the first place is a necessity dictated by the need to maintain parallelism after gel swelling, the latter amplifying all sorts of defects. The principle of the method relies upon injection-molding in a cylindrical mold. A homogeneous solution is obtained first by heating at 150 °C under sporadic stirring. As was detailed elsewhere,⁶ no noticeable chemical degradation occurs under these conditions. A piece of gel prepared through a quench at 20 °C of the solution is transferred into a syringe, heated up again at 150 °C, and finally injected into the mold, the latter being also kept at 150 °C. Finally the system is quenched at 20 °C while an adequate pressure is maintained manually on the syringe to compensate for volume shrinkage taking place during cooling. Examination between crossed polarizers indicates that this preparation method does not induce much orientation as the sample is only slightly birefringent near the injection hole. For each solvent three samples were prepared.

This preparation procedure allows determination of the modulus to within $\pm 5\%$ and is independent of the experimentalist, all things being equal. In particular, it is not sensitive to the pressure applied by the experimentalist while cooling the system. The results given here correspond to the average value on the three samples.

In the present study gels obtained at only one concentration have been investigated, namely, 0.175 g/cm³.

Dilute solutions (0.5 $\times 10^{-2}$ g/cm³) were prepared at 150 °C and aged at 20 °C for the same time as needed for the gel to reach equilibrium.

(3) **Gel Swelling.** All samples have been immersed in an excess of preparation solvent to achieve equilibrium swelling. The swelling kinetics was followed by measuring the sample's weight until equilibrium was reached (or nearly reached). The

Table I
Characteristics of the Solvents (abbrev = Abbreviation, Chemical Formula, Molar Volume) together with the Characteristics of the Gels Prepared from These Solvents (Equilibrium Swelling Ratio and Compression Modulus)

solvent	abbrev	chem form	V_m (cm ³ /mol)	$G_{v\infty}$	modulus (kPa)
dibutyl oxalate	DBO	C ₁₀ H ₁₈ O ₄	205	2.55	4.0
dibutyl succinate	DBS	C ₁₂ H ₂₂ O ₄	235	2.24	4.95
dibutyl adipate	DBA	C ₁₄ H ₂₆ O ₄	269	2.44	5.0
dibutyl sebacate	DBSU	C ₁₈ H ₃₀ O ₄	302	2.18	6.1
diethyl oxalate	DEO	C ₆ H ₁₀ O ₄	136	1.04	17.7
diethyl malonate	DEM	C ₇ H ₁₂ O ₄	152	0.9	22.4
diethyl succinate	DES	C ₈ H ₁₄ O ₄	166	1.11	14.3
diethyl glutarate	DEG	C ₉ H ₁₆ O ₄	184	1.85	6.5
diethyl adipate	DEA	C ₁₀ H ₁₈ O ₄	201	1.74	8.8
diethyl pimelate	DEPI	C ₁₁ H ₂₀ O ₄	218	1.86	6.5
diethyl suberate	DESU	C ₁₂ H ₂₂ O ₄	235	2.04	6.1
diethyl azelate	DEAZ	C ₁₃ H ₂₄ O ₄	251	1.99	7.2
diethyl sebacate	DESB	C ₁₄ H ₂₆ O ₄	268	1.77	8.1
diethyl dodecanedioate	DED	C ₁₆ H ₃₀ O ₄	301	1.62	9.6
isoamyl acetate	IA	C ₇ H ₁₄ O ₂	149	2.06	3.2
ethyl valerate	EVA	C ₇ H ₁₄ O ₂	149	1.82	5.4
ethyl caproate	ECRO	C ₈ H ₁₆ O ₂	166	1.43	8.7
ethyl heptanoate	EH	C ₉ H ₁₈ O ₂	181	1.31	11.8
ethyl caprylate	ECRY	C ₁₀ H ₂₀ O ₂	198	1.13	17.6
ethyl pelargonate	EPL	C ₁₁ H ₂₂ O ₂	215	1.03	22.2
ethyl caprate	ECP	C ₁₂ H ₂₄ O ₂	232	0.94	29.7

swelling ratio, $G_{v\infty}$, was defined as the ratio of the sample's final volume, V_∞ , to the sample's initial volume, V_0 , and was obtained by means of a profile enlarger. The accuracy on the determination of $G_{v\infty}$ can be estimated to be better than $\pm 5\%$.

(4) **Mechanical Testing.** Compression modulus measurements as well as compression stress relaxation experiments were carried out with a device described elsewhere.⁸ The investigations were performed on samples swollen to equilibrium. The gels were kept immersed in the preparation solvent which was thermostatically monitored to $20 \pm 0.5^\circ\text{C}$ by an outer water circulation. As usual the compression modulus (static or isochrone) was calculated after the relation

$$E = - \frac{P}{A_0(\lambda - 1/\lambda^2)} \quad (1)$$

in which P is the force resulting from a strain λ ($\lambda = l/l_0$, l_0 is the sample's initial height and l the displacement) on a sample of initial area A_0 . The compression modulus E is one-third of Young's modulus.

(5) **DSC.** Differential scanning calorimetry experiments were carried out with a DSC-7 device from Perkin-Elmer. Approximately 10 mg of gel was placed into a "volatile sample" pan and heated at a rate of $20^\circ\text{C}/\text{min}$. Calibration was achieved with indium and gallium. The pan was then heated up to 150°C , cooled down to 20°C , and aged appropriately prior to any measurements.⁶

(6) **Light Scattering.** Light scattering experiments were carried out on dilute PVC solutions in the various solvents. These solutions were contained in an "optical glass" cell immersed in a thermostatic bath held at $20 \pm 1^\circ\text{C}$. Three different baths were used to estimate errors from stray light arising from the mismatch of the solution refractive index and the glass's: toluene ($n_D = 1.4965$), water ($n_D = 1.33$), and dioxane ($n_D = 1.4215$).

The solutions were irradiated by an argon laser beam ($\lambda_0 = 488\text{ nm}$).

Results and Discussion

(1) **Swelling Experiments.** Typically, two types of swelling behavior are seen, depending upon whether the gel has been prepared with a monoester or with a diester (see Figures 1 and 2). In a monoester the swelling rate (dG/dt) is very rapid at the early stage and goes through a maximum at about 2 days followed by a decrease of

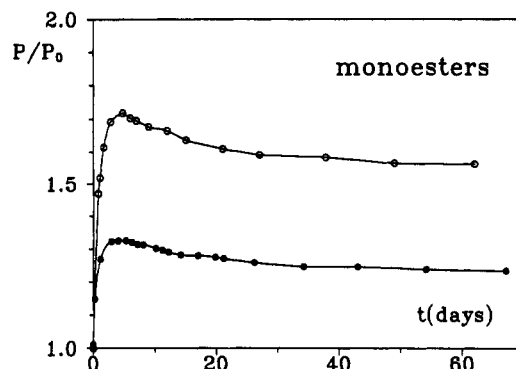


Figure 1. Evolution of the swelling ratio as a function of time (in days) for gels prepared from monoesters: (O) gels from ethyl caproate; (●) gels from ethyl caprylate.

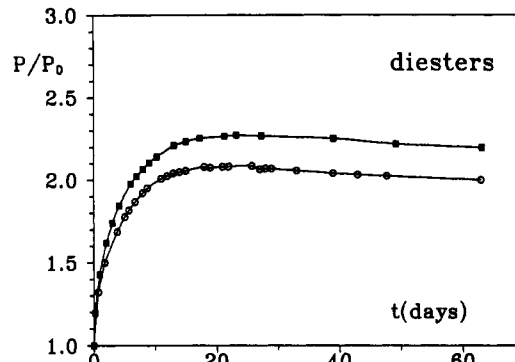


Figure 2. Evolution of the swelling ratio as a function of time (in days) for gels prepared from diesters: (■) gels from dibutyl succinate; (O) gels from diethyl pimelate.

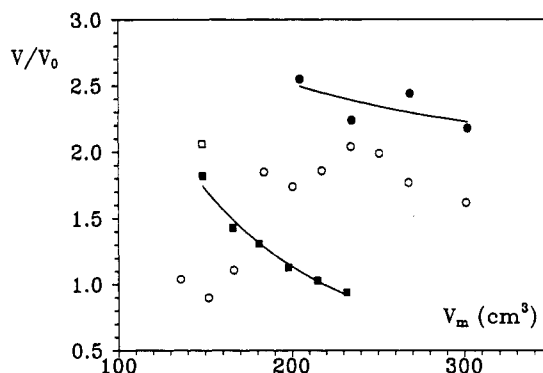


Figure 3. Variation of the equilibrium swelling ratio after 52 days as a function of the solvent molar volume: (O) diethyl esters, (●) dibutyl esters; (■) ethyl esters; (□) isoamyl acetate. Solid lines are only guides for the eye.

about 10% before reaching equilibrium. In a diester the swelling rate is lower than that in a monoester. No similar maximum as in monoesters is seen, although after about 20 days there is a slight decrease. In both systems a quasi-equilibrium is attained after 52 days.

Interestingly enough, if the swelling equilibrium ratio, $G_{v\infty} = V_\infty/V_0$ (in which V_0 and V_∞ are the original volume and the volume reached at equilibrium), is plotted as a function of the solvent molar volume, then a difference is again observed between diesters and monoesters (see Figure 3). In *monoesters*, the degree of swelling decreases with increasing solvent molar volume. The monoester molecules of a smaller size lead to the highest degree of swelling. Besides, at equivalent molar volume, isoamyl acetate, the monoester which contains the larger alcohol group, leads to a significantly higher degree of swelling than ethyl valerate. Conversely, in *diesters*, there seems to be two types of behavior: for diesters of low molar volume the degree of swelling is close to 1 while it goes up

to about 1.7–2 for diesters of $V_M > 180 \text{ cm}^3/\text{mol}$. Here, one observes a slight decrease with increasing molar volume, but in no case something comparable to what is seen in diesters. Of further note is the increase of swelling power when the alcohol substituent is changed from ethyl to butyl. Dibutyl oxalate leads to markedly higher degrees of swelling than diethyl oxalate does. As a rule, the dibutyl diesters investigated lead always to higher degrees of swelling than diethyl esters at equivalent molar volume.

It seems worth examining these different types of behavior in the light of the possible PVC–solvent interactions. In this aim, it is of interest to consider the investigations carried out by Tabb and Koenig⁸ and later by Monteiro and Mano.⁹ These authors conclude that there exists a specific interaction that leads to complex formation between the carbonyl group of these solvents ($\text{C}=\text{O}$) and the $\text{H}-\text{C}-\text{Cl}$ part of the PVC chain. This interaction is quite easily accounted for if one realizes that the $\text{C}=\text{O}$ bond is polarized so as to give a negative “fractional” charge on the oxygen atom, $\text{C}=\text{O}^\delta$, while the $\text{H}-\text{C}-\text{Cl}$ is also polarized so as to give a positive fractional charge on the hydrogen, $^\delta\text{H}-\text{C}-\text{Cl}^\delta$.^{10,11} Accordingly, PVC–ester interaction might mainly arise from electrostatic effects. This scheme was already suggested by Kratochvil et al.¹² to account for PVC solubility in some solvents. Obviously, the higher the polarization of the $\text{C}=\text{O}$ bond, the larger the fractional charge and the stronger the interaction. The results presented here are consistent with this scheme. As a matter of fact, it is known that the $\text{C}=\text{O}$ polarization increases with increasing the size of the alcohol substituent but also, to a lesser extent, the size of the acid part. So, it is expected that dibutyl esters interact more strongly with PVC than diethyl esters do, which one does experimentally observe through the degree of swelling.

The different types of swelling behavior versus the solvent molar volume, depending upon whether a diester or a monoester is used, deserve a short discussion. If the PVC–ester interaction is mainly governed by the electrostatic interaction described above, then any screening of the carbonyl group will considerably attenuate it. Increasing the length of the acid substituent in a monoester may promote such a screening, as this aliphatic part is liable to coil around the carbonyl group. This screening effect may cancel out the enhanced polarization of the $\text{C}=\text{O}$ bond. In contrast, this type of screening is less likely to occur with a diester, even by increasing the length of the acid substituent, as it would imply forcing two carbonyl groups carrying the same type of electrostatic charge to come closer. Such a mechanism can account for why the degree of swelling decreases considerably with increasing the size of a monoester while there is little effect with a diester when the alcohol group is kept the same.

(2) Mechanical Behavior. In a first series of experiments the stress relaxation at constant deformation has been examined. As a rule, the stress relaxation has been found to vary as

$$\sigma_R \approx t^{-m} \quad (2)$$

in which m stands somewhere between 0.005 and 0.03. From Figure 4, it seems that two regimes can be distinguished: for high degrees of swelling $m \approx 0.005$, while for low degrees of swelling $m \approx 0.02$ –0.03. Monoesters and diesters are not distinguishable here. PVC gels do relax like chemical gels, as was already reported elsewhere.⁶

As there is little relaxation, these gels can be studied by varying the deformation and measuring a compression modulus as given by relation 1.

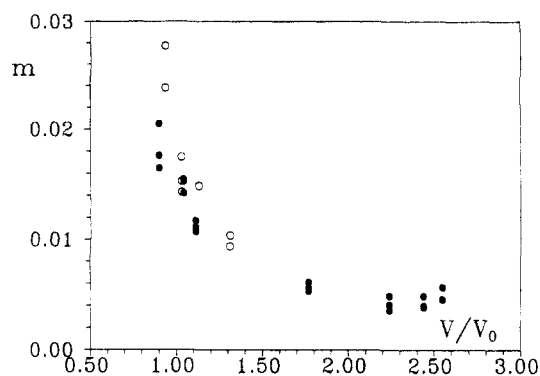


Figure 4. Variation of the relaxation rate, m (from $\sigma_R \approx t^{-m}$), as a function of the equilibrium swelling ratio: (●) diesters; (○) monoesters.

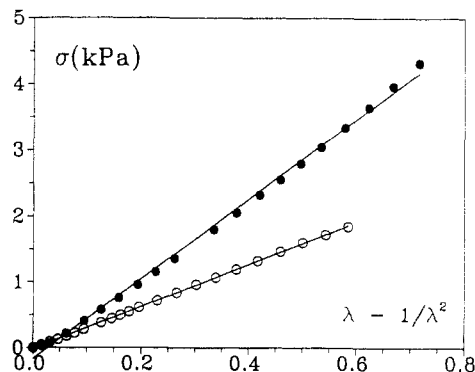


Figure 5. Typical plots of σ vs $\lambda - 1/\lambda^2$: (○) gel from isoamyl acetate; (●) gel from diethyl suberate.

As can be seen in Figure 5, straight lines are observed when plotting the stress σ versus $\lambda - 1/\lambda^2$. The use of samples possessing faces as parallel as possible allows one to obtain a very low residual stress σ_0 when extrapolation to $\lambda - 1/\lambda^2 = 0$ is made. Generally, samples with poorly parallel faces yield a high value for σ_0 (negative value) when extrapolation is achieved in the linear part of the data. As a result, the parallelism of the sample's faces can be evaluated by considering the ratio $\epsilon = |\sigma_0|/E$. Samples with highly parallel faces should give $\epsilon \approx 0$. In all the samples investigated in this study this ratio has always been lower than 0.03.

(3) Modulus versus Swelling. Investigation into the variation of the modulus as a function of swelling and the related conclusions rely upon the following rationale: if only crystalline links formed with the syndiotactic sequences are present, then, at same solvent quality, the modulus should be the same for samples of the same concentration irrespective of the solvent type. In other words, gels prepared at the same concentration which swell to the same extent possess the same number of crystalline links per unit volume and, ultimately, the same modulus. This point is worth discussing in light of Flory's relation for the melting point depression, ΔT ,¹³ which allows calculation of the liquidus line

$$\frac{\Delta T}{T_{mp} T_{mp}^0} = \frac{R V_p}{\Delta H_{op} V_s} [(1 - v_p) - \chi_1 (1 - v_p)^2] \quad (3)$$

in which T_{mp} and T_{mp}^0 are the actual melting point of the solid solution and of the pure polymer, V_s and V_m are the molar volumes of the solvent and the monomer, respectively, v_p is the polymer volume fraction, χ_1 is Flory's parameter of interaction, and ΔH_{op} is the melting enthalpy of the pure polymer. Knowledge of the liquidus line allows determination of the proportion of crystalline material at a given temperature (see Figure 6).

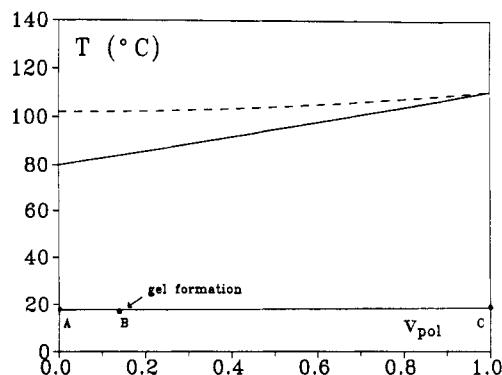


Figure 6. Theoretical liquidus lines for PVC crystallites possessing a melting point of $T_m = 110^\circ\text{C}$ in the bulk state. The solid line stands for $V_s = 150\text{ cm}^3/\text{mol}$ and $\chi_1 = 0$ while the dashed line stands for $V_s = 300\text{ cm}^3/\text{mol}$ and $\chi_1 = 0.5$. Gel formation is indicated. The amount of crystalline phase in this diagram is given by the lever rule, i.e., BA/AC.

Table II

Value of δT ($\delta T = T_{mp} - 293\text{ K}$) Calculated by Means of Relation 3 by Using $\Delta H_{op} \approx 2800\text{ cal/mol}$, $T_{mp}^\circ = 110^\circ\text{C}$, $V_p = 46.6\text{ cm}^3/\text{mol}$, and $v_p = 0.13$

χ_1	$V_s = 150$	$V_s = 300$
0	63	76
0.5	74	82

In relation 3 two parameters are related to the solvent type: χ_1 and V_s . Strictly speaking, the above rationale holds true only if the solvents also possess the same molar volume. As has been seen in the previous section this is not necessarily the case when comparing solvents giving the same degree of swelling, particularly between esters and diesters. It is therefore of prime importance to find out to which extent the above rationale can be regarded valid for the present study.

The lever rule indicates that for a given temperature the higher the undercooling, the largest the amount of crystalline materials. Now, if one considers the same concentration and the same interaction parameter, χ_1 , it can be straightforwardly shown that the larger the solvent molar volume, the higher the undercooling. As a result, solvents of higher molar volume should yield a larger amount of crystalline materials, and if this crystalline material constitutes the physical junctions, then more links should exist. In fact this is true when the temperature is close to the melting temperature (low undercoolings). At large undercoolings, however, all the crystallizable material tends to be crystallized (see Figure 6) so that the only relevant parameter to the problem remains χ_1 . In the case of PVC a numerical calculation of the melting point for the less perfect crystallites (onset of pure PVC melting endotherm at about 110°C ¹⁴) can be achieved at the concentration used in this study by considering the following parameters: $T_{mp}^\circ = 110^\circ\text{C}$, $V_s = 150\text{--}300\text{ cm}^3/\text{mol}$, $V_m = 46.6\text{ cm}^3/\text{mol}$, $v_p = 0.13$ (taking $\rho_{PVC} = 1.4\text{ g/cm}^3$), and $\chi_1 = 0.5$ and 0. The results obtained for the undercooling, δT , at $T = 20^\circ\text{C}$ ($\delta T = T_{mp} - 20^\circ\text{C}$) are gathered in Table II and the limiting cases drawn in Figure 6. Clearly, the calculated undercoolings, δT , are rather large. It can be safely concluded that the samples under study have been crystallized, at 20°C and at constant interaction parameter χ_1 , to virtually the same extent.

That mainly the interaction parameter is involved is illustrated experimentally in the case of diesters. Inspection of Table I, wherein are given the compression moduli together with the degrees of swelling, reveals that samples of nearly identical degrees of swelling possess moduli

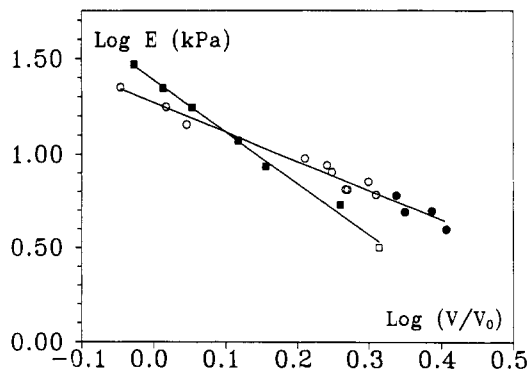


Figure 7. Variation of the modulus as a function of the equilibrium swelling ratio in a logarithmic representation: (■) ethyl esters; (□) isoamyl acetate; (○) diethyl esters; (●) dibutyl esters.

virtually the same (case of gels in DEA and gels in DESB) despite the large discrepancy of molar volumes.

Experimental results reveal noticeable discrepancies between monoesters and diesters. Consequently, we shall conclude that phenomena other than simple crystallization take place. Figure 7, wherein the moduli are plotted as a function of the degree of swelling in a double-logarithmic scale, emphasizes the two types of behavior. The following relations are obtained:

$$\text{monoesters} \quad E = 24.5 G_{v_s}^{-2.72 \pm 0.1} \text{ kPa} \quad (4)$$

$$\text{diesters} \quad E = 18.6 G_{v_s}^{-1.54 \pm 0.1} \text{ kPa} \quad (5)$$

These results point at the existence of *two classes of universality*: one in diesters and one in monoesters, irrespective of the alcohol substituent. Dibutyl and diethyl fall on the same line as do ethyl and isoamyl.

Also, relations 4 and 5 do emphasize the difference that exists between chemical gels, the elasticity of which is of entropic origin, and PVC thermoreversible gels. For chemical gels the variation of the modulus as a function of the swelling degree obeys power laws yet with exponents far smaller. For instance, results obtained by Belkebir-Mrani et al. for PDMS gels in different solvents give exponents of about 0.23.¹⁵ Bastide et al. have determined an exponent of about 0.5 for polystyrene gels submitted to osmotic deswelling.¹⁶ Rogovina et al. report exponents between 0.5 and 0.8.¹⁷ In no case exponents larger than 1 are found. It is to be noted that in the case of chemical gels swelling essentially results in diluting the number of junctions per unit volume. Evidently, in both *diesters* and *monoesters* additional effects occur.

Interestingly enough, while for a high swelling ratio moduli of gels prepared from diesters are effectively higher than those from monoesters, the reverse situation is seen for a low swelling ratio, the inversion occurring in the vicinity of $G \approx 1.3$.

(4) Molecular Interpretation. The above results suggest that the molecular structures of either type of gel differ. To give further support to this statement, light scattering experiments have been carried out on pregels, i.e., aggregates formed below the critical gel concentration. The aggregates have been prepared at a concentration of $0.5 \times 10^{-2}\text{ g/cm}^3$. They have also been aged 52 days prior to measurements. Typical scattering patterns are drawn in Figures 8 and 9. Intensities are given in arbitrary units. Figure 8 corresponds to solvents in which gels do not swell (actually deswell slightly), whereas Figure 9 corresponds to solvents in which strong swelling is observed. As can

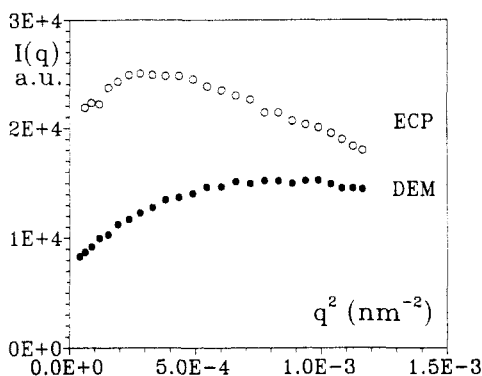


Figure 8. Intensity (in arbitrary units) scattered by aggregates ($C = 0.5 \times 10^{-2} \text{ g/cm}^3$) as a function of the square of the transfer momentum $q = 4\pi n_s/\lambda_0 \sin(\theta/2)$ where n_s is the solvent's refractive index and λ_0 the incident wavelength (488 nm): (O) ethyl caprate (ECP); (●) diethyl malonate (DEM).

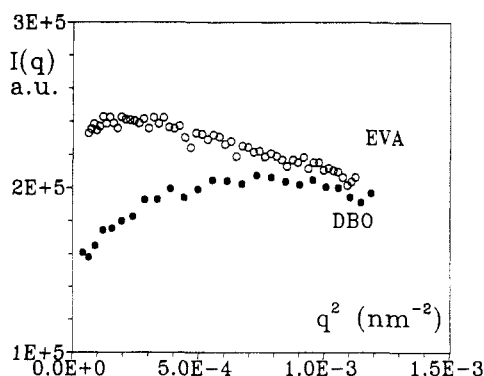


Figure 9. Intensity (in arbitrary units) scattered by aggregates ($C = 0.5 \times 10^{-2} \text{ g/cm}^3$) as a function of the square of the transfer momentum $q = 4\pi n_s/\lambda_0 \sin(\theta/2)$ where n_s is the solvent's refractive index and λ_0 the incident wavelength (488 nm): (O) ethyl valerate (EVA); (●) dibutyl oxalate (DBO).

be seen, aggregates prepared from diesters exhibit a pattern different from those prepared from monoesters. In *diesters* one observes a prominent downturn at small angles together with a broad maximum at large angles, a result already reported by Mutin and Guenet.¹⁸ The pattern is essentially independent of the solvent's quality. Conversely, in *monoesters* there is a maximum at small angle, quite conspicuous with ethyl caprate while less marked with ethyl valerate, whose position seems to shift to lower q -values as the solvent's quality increases.

These experiments do show that the aggregate molecular structure differs whether monoesters or diesters are dealt with. It further suggests that the molecular structure is little sensitive to the solvent's quality in diesters while it seems to be in monoesters.

Another point of interest deals with the reason why gels prepared from monoesters possess moduli higher than those prepared from diester at a low swelling ratio. This seems contradictory with the existence of additional links in diesters only. For the purpose of accounting for this paradox, we shall consider the fiberlike structure as observed by Yang and Geil from electron microscopy¹⁰ and later given support by Abied et al.⁷ Also, it is worth keeping in mind that low swelling ratios are found with monoesters of highest molar volume, whereas the reverse situation is seen for diesters.

In what follows we shall consider essentially that gels from monoesters possess a type of elasticity which is *enthalpic* at a low swelling ratio and becomes *entropic* at a high swelling ratio. Conversely, we shall regard elasticity in diester gels as being always chiefly *enthalpic*.

In Figure 10 are portrayed fiberlike models. At a *high swelling ratio* the solvent molecules can enter the non-

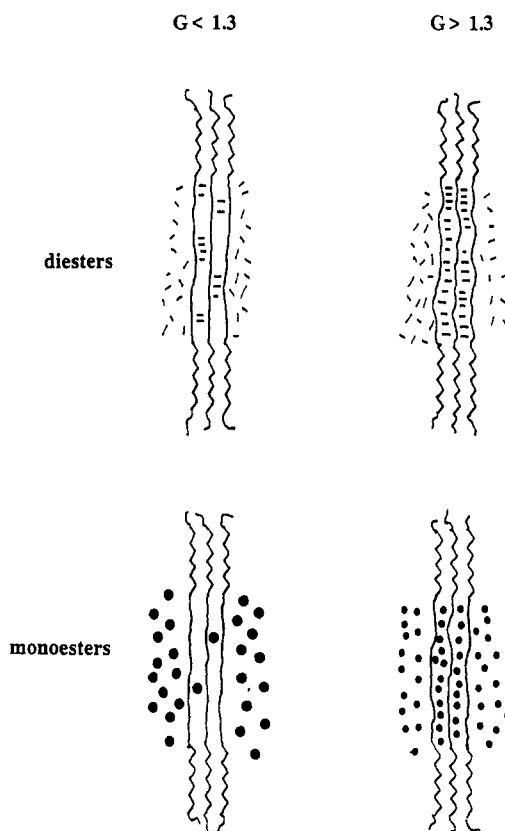


Figure 10. Schematic representation of a fibril containing crystalline zones composed of syndiotactic sequences (zigzag lines) and noncrystalline zones. Diesters are represented with dashes in order to indicate their capability of forming bridges between chains, while monoesters are represented with filled circles.

crystalline domains, more especially so as these domains show affinity with the solvents. Diesters form additional links, while monoesters do not. At a *low swelling ratio* the noncrystalline domains do not tend to absorb much solvent. Access to these domains is probably restricted. While diesters can still enter these domains thanks to their small size, and accordingly form additional links, it is quite likely that monoesters cannot do so as easily since they are far bigger. As a result, in the latter case the noncrystalline domains being poorly solvated are liable to stand below their glass transition temperature. If such is the case, then fiberlike structures in monoesters giving low swelling ratios should be rigid and accordingly display *enthalpic elasticity*. This may result in considerable modulus reinforcement. The drop of the modulus with the swelling ratio observed in monoesters would then primarily arise from plasticization effects, going from a very rigid object to flexible structures. This would entail a kind of transition from *enthalpic* to *entropic* elasticity.

If the above view is correct, then gel thermal behavior should differ whether monoesters or diesters are used. In diesters some kind of endotherm should be visible, representing the melting of the additional links. This endotherm has already been observed in diethyl malonate⁶ at about $T = 55^\circ \text{C}$. Alternatively, in monoesters giving low swelling ratios the occurrence of a glass transition is expected.

The validity of these statements has been tested by thermal analysis (DSC). Results are reported in Figure 11. As can be seen, one does observe a glass transition in ethyl pelargonate gels, the midpoint of which is located at $T = 30 \pm 1^\circ \text{C}$, whereas a melting endotherm occurs in diethyl oxalate gels, the maximum of which lies near $62 \pm 2^\circ \text{C}$.

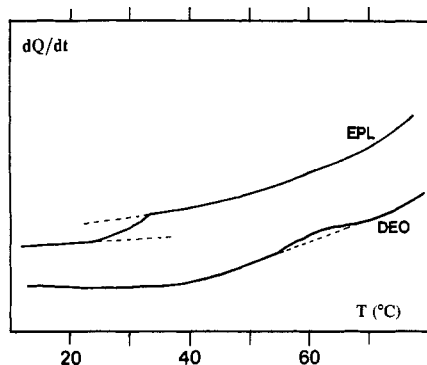


Figure 11. Thermograms recorded with ethyl pelargonate gels (EPL) and diethyl oxalate gels (DEO). In both cases $C = 0.175$ g/cm³ and the heating rate is 20 °C/min. dQ/dt is in arbitrary units.

(5) **Theoretical Approach.** It seems worthwhile to compare the present experimental results to theories dealing with rigid networks for which *enthalpic* elasticity dominates. We shall use the approach recently derived by Jones and Marquès.¹⁹ For rigid objects joining the junction domains these authors express the modulus E as

$$E \approx \frac{er^4n}{N^{3\nu+1}a^4} \quad (6)$$

in which e is the material intrinsic Young's modulus, r the cross-section radius, n the functionality of the junctions, and $N^\nu a = R$ the end-to-end distance of the rigid object. In the latter relation, $1/\nu$ is nothing more than the fractal dimension of the object. This approach can be generalized to systems composed of fibrils by making the following assumptions:

(i) The end-to-end distance of the fibril is larger than its cross-sectional radius ($R > r$).

(ii) The junction domains are small compared to the network mesh size.

(iii) The fractal dimension to take into consideration is related to the longitudinal length of the fibril.

To derive a relation modulus–swelling ratio, we shall make further assumptions. We shall consider that the fibril fractal dimension as defined in iii does not vary with swelling. Only a , which stands for the fibril persistence length, is assumed to increase with increasing swelling.

We shall therefore consider a reference state, which basically corresponds to the case where there is no swelling (N_0 , R_0 , and a_0). Finally, we shall write the swelling ratio as

$$G_v \approx (R/R_0)^3 \quad (7)$$

Keeping in mind that the longitudinal contour length of the fibril ought to be a constant ($Na = N_0a_0$), the following relation is derived after some simple algebra:

$$E \approx \frac{er^4n}{N_0^{3\nu+1}a_0^4G_v} \quad (8)$$

This relation indicates that $E \approx G_v^{-1}$ which is lower than the exponent 1.54 found with diesters for which this

type of analysis may pertain. Here, we have considered that the cross-section radius is constant. This may not be the case. It would suffice that this parameter varies like $G_v^{-0.135}$ to account for the 1.54 value.

Conversely, relation 8 is inappropriate for gels in monoesters. Probably, an approach considering plastification effects may be far more suited.

Concluding Remarks

In this paper we have clearly shown the effect of the solvent type on the gelation mechanism and structure of PVC gels. The relation modulus–swelling depends strongly upon whether monoesters or diesters are used. So do the long-range molecular structure as well as the thermal behavior. Mutin and Guenet's suggestion received accordingly further support. The methods of investigation described herein only provide, however, circumstantial evidences. It now remains to demonstrate directly, possibly by spectroscopic techniques, the involvement of the solvent in the gel structure. Complementary experiments by dynamic light scattering are in progress to cast more light on the aggregate structure.

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