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Effect of solvent on glass transition temperature in chemically modified polyvinyl chloride (PVC)

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Abstract: Polyvinylchloride has been chemically modified with sodium benzene thiolate at different temperatures, in solvents promoting the formation of polymer gels, in solvents favoring light polymer interactions and in the absence of solvent, that is, in the melt. From the ^{13}C-NMR results it is shown that the substitution reactions on PVC, in all media and temperatures studied, are stereospecific and the nature of substituted chlorines the same.

The glass transition temperature of modified polymers has been studied by differential scanning calorimetry. The glass transition temperature of the modified polymers in the absence of solvent decreases linearly with degree of substitution. When the reaction is carried out in solvents containing carbonyl groups, such as diethyl malonate, cyclohexanone and 2-butanone, the evolution of the glass transition up to about 25% substitution does not follow the above behavior. At higher levels of substitution the evolution of T_g is similar to that in the melt. For the ether-containing solvents, such as tetrahydrofurane and dioxane, the evolution lies between the two previous curves.

When the reactions of PVC with sodium benzene thiolate are carried out in cyclohexanone at different temperatures, between 15–90 °C, the evolution of the glass transition temperature with conversion is different for each temperature, and if the reaction temperature increases, the slope of the initial part moves to that in the absence of solvent.

These results are related to the formation of PVC gels or interactions. As the nature and percentage of substituted chlorine for a given chemical composition are the same in all the solvents and conditions studied, we propose that Cl-atoms of isotactic and/or heterotactic configurations are implied in the formation of PVC gels or interactions.

Key words: PVC – interactions – polymer reactions – glass transition – influence of solvent – stereoselectivity

Introduction

PVC gels

When it is attempted to dissolve PVC in certain solvents, formation of gels, associations or intermolecular complexes occur, and unequivocal evidence has been presented in recent work by Guenet et al. [1–6], Maddams et al. [7–10], Chalykh et al. [11], Santamaria et al. [12, 13], and others [14–19]. For instance, Challykh et al. observe that in the PVC-2 butanone system, two types of gels are formed. One type of supramolecular structure is broken down and another type is formed due to the stabilization of non-equilibrium PVC conformations by solvation. Jackson and Maddams et al. studied the gel formation in PVC/cyclohexanone and PVC/dioctyl phtalate systems associated in the first case with hydrogen bonding. In the last system, PVC/DOP, Santamaria et al. proposed the formation of gels due to the participation of links (i.e., formation of complexes between PVC and the solvent, as suggested by Guenet et al.), besides crystallites in the formation of the structure of aged gels. Dorrestijn et al. [14–16] studied the gelation of PVC and chlorinated PVC in DOP and reported that a 13% molar concentration of additional chlorines introduced by random chlorination in solution completely suppresses gelation, which is in contrast with bulk chlorinated samples, and they ascribed the difference to the influence of intramolecular chlorine distribution on crystallizability. Guenet et al. have shown that in PVC/bromonaphthalene, PVC-diethyl malonate systems and others, the solvent type has an important influence and can, in particular, play a role similar to that of an increase in syndiotacticity, that is, promoting the formation of additional, less stereoregular links. These results are all discussed in terms of polymer-solvent interactions.

PVC reactions

The chemical modification of PVC allows one to not only improve the original properties of the polymer, but also to study the polymer structure after a controlled substitution, when the obtained polymer is compared with the original one. In this respect, we have extensively studied the substitution reactions of PVC with different nucleophilic reactants in cyclohexanone solution, in aqueous suspension with a phase transfer catalyst, and in the melt, in a continuous or discontinuous process [20–28].

Previous work stated that nucleophilic substitution on PVC is stereospecific and the reactions only takes place at Cl atoms of isotactic and heterotactic triads in the media studied.

The substitution reactions on PVC carried out in different solvents and media, going from gel-forming-solvents to the absence of solvent, bring about, on the one hand, the possibility of the formation of polymer-solvent and polymer-polymer interactions that can originate additional links in the modified polymer structure and, on the other, the gradual elimination of specific chlorine atoms.

PVC properties

Different properties of PVC gels have been determined by several techniques [1–19] including microscopy, simple rheological measurements, dynamic viscoelastic measurements, differential scanning calorimetry and light scattering.

Molecular motions must change if some new links or interactions are introduced, and as T_g in the polymer is associated with long-range molecular motions, the comparison of T_g for modified PVC in different media, leading to specific interactions or not, can provide indirect information about the structure involved in the polymer-solvent interactions.

This first paper examines the influence of interactions of PVC-solvent on the glass transition temperature, and proposes stereospecific reactions on the polymers as a method to study the type of chlorine involved in the interactions' PVC/solvent.

Experimental

Materials

Commercial block-polymerized PVC was obtained from Rio Ródano Industries, Spain. The average molecular weights obtained in a Waters GPC chromatograph are $M_w = 112\,000\ \mathrm{g\,mol^{-1}}$, $M_n = 48\,000\ \mathrm{g\,mol^{-1}}$, and the tacticity measured by ^{13}C-NMR is syndio = 30.7, hetero = 49.8 and iso = 19.6.

The sodium benzene thiolate (NaBT) was a commercial product from Fluka, n° 89027. Cyclohexanone was bidistilled prior to use. Dioxane and tetrahydrofurane were also distilled. Diethyl malonate and 2-butanone were of high purity grade commercial solvents.

Substitution reactions

Substitution in different solvents and media: The substitution reaction of PVC, 2 g, with sodium benzene thiolate, 4.22 g, was carried out in 250 cc of cyclohexanone (CH) at 60 °C. At appropriate reaction time samples were withdrawn, precipitated immediately in methanol, purified with THF-MeOH as the solvent-precipitant system, and dried at 40 °C under vacuum for 2 days. The samples were analyzed by a method described elsewhere [25].

The same protocol was followed for butanone (BU), tetrahydrofurane (THF), and diethyl malonate (DEM).

The substitution reactions of PVC in dioxane (DX) and aqueous suspension were carried out under the same conditions as above with the aid of tetrabutylammonium bromide as phase transfer catalyst in a proportion of 1 : 0.05 nucleophile/catalyst. Due to heterogeneous reaction of PVC in water with tetrabutylammonium bromide, each sample was obtained by a different reaction.

The substitution reaction of PVC in the melt was carried out in a Brabender Plasticorder system in the following conditions. PVC = 100 g, NaBT = 56.25 g, plasticizer = 30 g, T = 160 °C and 40 rpm. At appropriate reaction times samples were withdrawn, purified and analyzed by a method described elsewhere [20].

Substitution at different temperatures: In order to study the effect of the temperature on the PVC/gel formation, substitution reactions of PVC with NaBT were also carried out both in cyclohexanone at + 15 °C, + 25 °C and + 90 °C and in diethyl malonate at 100 °C in the same conditions to that of 60 °C.

NMR characterization

The stereochemical structure of substituted PVC in different solvents was studied by ^{13}C-NMR spectroscopy at 75.5 MHz in deuterated dioxane at 90 °C in a 300 MHz XL-Varian Spectrometer in conditions previously described [20–25]. The resonances used are those of the methynic carbons of unreacted chlorines, ranging from 57.0 to 60.0 ppm, which give the relative proportions of isotactic, heterotactic, and syndiotactic triads. The information concerning ^{13}C-NMR signals of the substituted polymer has already been given. Figure 1 shows the spectra of the original and the PVC modified in the cyclohexanone at 11.3 and 25.0% molar conversion. The tacticity calculations were carried out using the integrals and by measuring the relative areas of the different peaks of methynic carbons with a compensating polar planimeter.

DSC measurements

The calorimetric measurements of solvent-free substituted PVC were carried out in a Perkin Elmer differential scanning calorimeter DSC-4, coupled with a thermal analysis data station. The DSC curves were obtained using 10 °C/min as heating rate after two runs of measurements from 0 to 150 °C. The reported T_g, taken from the final run, corresponds to the midpoint of the DSC curves measured from the extension of the pre- and post-transitions base line. As an example, the thermograms of PVC substituted with NaBT in cyclohexanone at 60 °C at different degrees of substitution are given in Fig. 2. The error in the measurement is ± 0.3 °C.

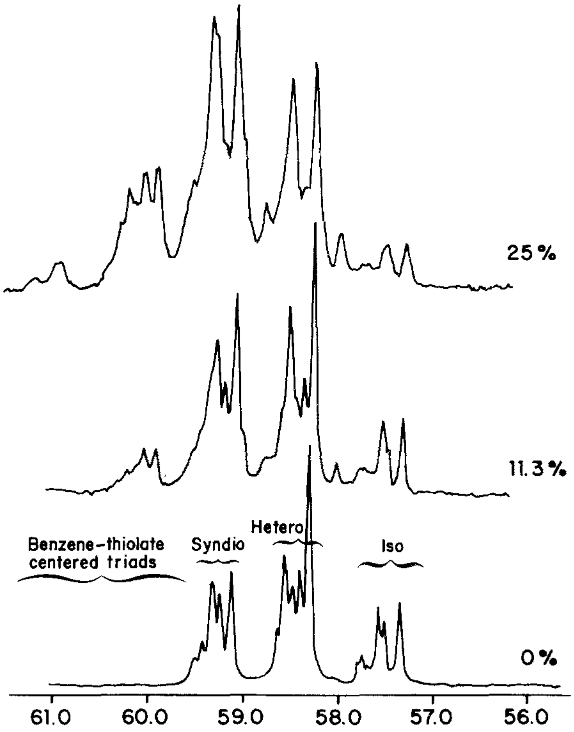

Fig. 1. Spectra of the PVC and PVC substituted with NaBT in CH at 11.3 and 25.0% molar composition

Results and discussion

In order to study the influence of the solvent and the nature of the chlorine on the formation of gels or interactions of polyvinyl chloride, substitution reactions of the polymer with sodium benzene thiolate in different solvents were performed. This study has been carried out under three different types of solvents: cyclohexanone, butanone and diethyl malonate as solvents with carbonyl groups or gel-forming-solvents; tetrahydrofurane and dioxane as solvents with ether groups, and in the absence of solvent, that is, in the melt.

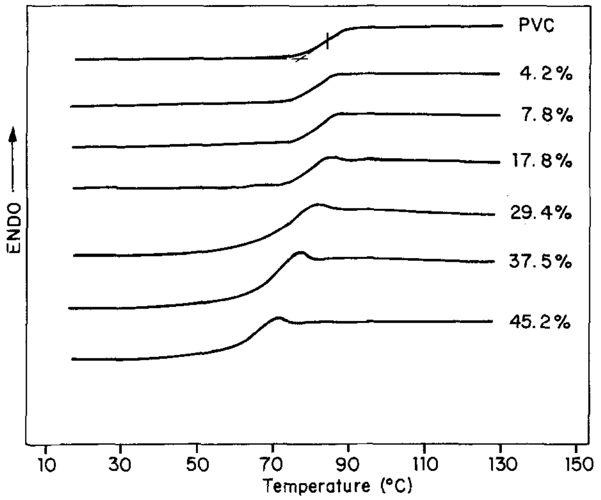

Fig. 2. Thermograms of PVC substituted with NaBT in CH at 60 °C to different molar composition

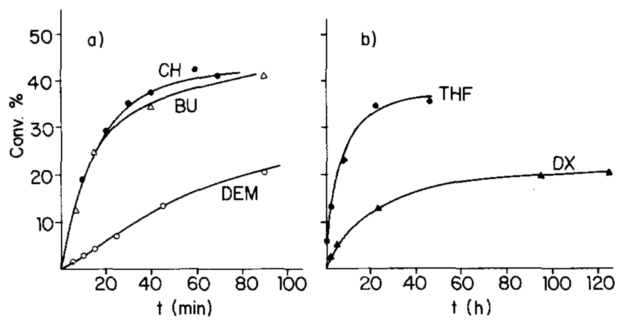

Fig. 3. Kinetic results of PVC reactions with sodium benzene thiolate, at 60 °C, in different solvents. a) carbonyl solvents: ●) cyclohexanone; △) 2-butanone; ○) diethylmalonate. b) ether solvents: ●) tetrahydrofurane; ▲) dioxane

The conversion-time curves for the substitution reaction of PVC with sodium benzene thiolate in CH, BU, DEM, THF, and DX at 60 °C are given in Fig. 3. In this figure it is observed that the reaction is faster and the degree of conversion higher for the solvents with larger dipole moments.

The stereostructural modification of PVC in solvents such as DX, THF, DEM, and BU has never been reported. In Fig. 4, the evolution of the content of the unreacted chlorine of isotactic, heterotactic, and syndiotactic triads with degree of the conversion for the modified polymer in the above solvents is shown. In this figure it is observed that the stereochemical evolution of the polymer for the same chemical compositions, in all the solvents studied, is the same. Clearly, the isotactic and heterotactic triads of unreacted chlorines decrease with increasing degree of substitution. The apparent increase in syndiotactic triads is due to the formation of a new β-substituted syndiotactic triad, as pointed out elsewhere [23–27].

On the other hand, a recent publication [27] reports that the evolution of isotactic, heterotactic and syndiotactic triads with degree of conversion for the reaction of PVC with the same reactive in cyclohexanone in the range of temperature 5–70 °C, similar to our study, is exactly the same. Moreover, the substitution reaction of PVC with the same reactant in the melt follows the same stereospecific mechanism as in cyclohexanone [20, 21, 26]. The ^{13}C-NMR results of these studies have been discussed at length [20–28] and have demonstrated that the substitution reaction in PVC only takes place at chlorines of isotactic and heterotactic configurations. Further, by Monte-Carlo simulation of the reaction kinetics and the evolution of modified polymer stereostructure, a value of almost zero has been found for the reactivity of the syndiotactic triads [24, 27].

Thus, we can say that in all the solvents and temperatures studied for the same chemical composition of the substituted polymer, the nature and the percentage of eliminated chlorine is the same, that is, that of isotactic and heterotactic chlorines.

Influence of the chemical composition on T_g

In order to ascertain the influence of the degree of conversion, or the chemical composition of the modified polymer on the glass transition temperature, the evolution of T_g with degree of conversion of the modified polymer in the absence of solvent is plotted in Fig. 5. From this figure it can be shown that the T_g value decreases linearly with degree of conversion. These results can be explained in terms of chemical composition, both by a decrease in the number of chlorine interactions in the PVC chains, as a consequence of substitution, and by the increased mobility of the newly formed unit. In fact, the high T_g value for PVC is attributed to chain-chain dipolar interactions of the chlorines, and the T_g of fully transformed

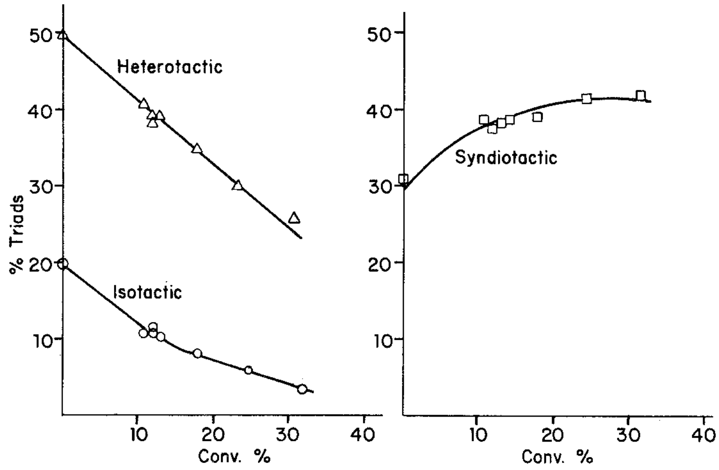

Fig. 4. Evolution of the relative content of isotactic (○), heterotactic (△), and syndiotactic (□) triads with degree of conversion for the reactions in tetrahydrofurane, dioxane, 2-butanone, cyclohexanone, and the aqueous suspension. The full lines correspond to the results previously reported in cyclohexanone solution and in the melt [19–26]

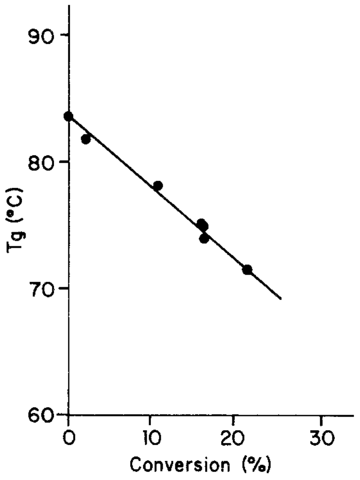

Fig. 5. Evolution of the glass transition temperature with degree of conversion for the reaction of PVC with sodium benzene thiolate in the absence of solvent (in the melt)

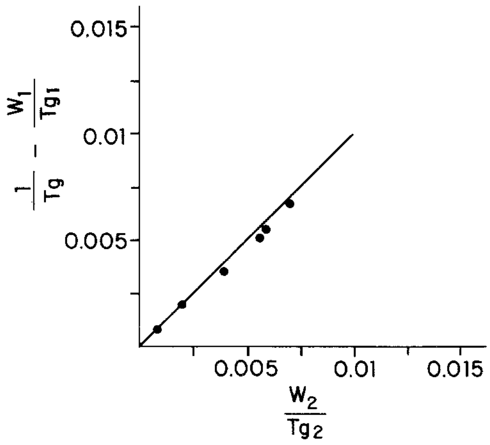

Fig. 6. Flory–Fox equation (—) and experimental points (●) of the melt modified polymer.

PVC into $-(-CH_2-CHS\phi-)-$ is 52.5 °C. Accordingly, in Fig. 6 the Flory–Fox equation of the newly obtained copolymers and the above experimental values are compared. It is found that the experimental data of the modified polymers fit the theoretical glass transition plot, thus indicating no other appreciable effect.

Influence of the solvent on T_g

If, as it has been stated, PVC in cyclohexanone can form gels [7–10], the modified PVC with NaBT in cyclohexanone should show a different T_g behavior from that in the absence of solvent. In Fig. 7, the evolution of T_g with degree of substitution for the PVC substituted in CH is compared with that of those modified in the melt. In this case there are two well differentiated behaviors. In the first part of the plot, up to about 25% conversion, the value of T_g is much higher than that which would correspond to chemical composition. Later, the evolution of T_g is similar to that found in the absence of solvent.

It is well known that T_g crucially depends on two important factors, chain flexibility and intermolecular interactions in the polymers. In our case, the first factor is exactly the same, since the ^{13}C-NMR spectra indicate the same microstructure,

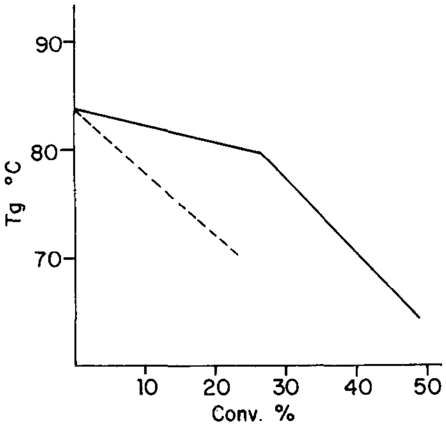

Fig. 7. Comparison of the glass transition temperature with degree of conversion for the reaction of PVC with sodium benzene thiolate in cyclohexanone (——) and in the absence of solvent (- - -)

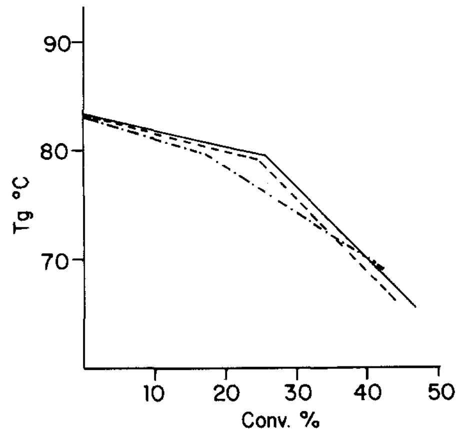

Fig. 8. Comparison of the glass transition temperatures with degree of conversion for the reaction of PVC with sodium benzene thiolate in different carbonyl solvents: butanone (—), cyclohexanone (- - -), diethylmalonate (- · -)

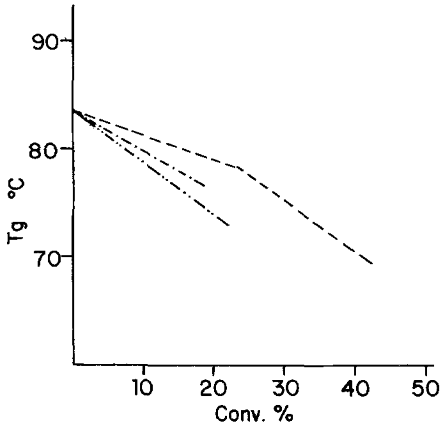

Fig. 9. Comparison of the glass transition temperatures with degree of conversion for the reaction of PVC with sodium benzene thiolate in different solvents: Tetrahydrofurane (- - -), dioxane (- · -) and aqueous suspension (- · · -)

thus only the second factor can be responsible for the different behavior. Thus, our results can be interpreted as if the solvent generates specific interactions or associations, on specific parts of the polymer, the nature of which will be discussed later, and is responsible for the high value of T_g, until a degree of conversion of about 25%. Then, the interactions begin to break down. It is reasonable to suppose that a concentration of 25% of new unities can break the ordered form or the new links formed on the polymer, so that it can recover the corresponding free or flexible form.

If that supposition is correct, when the reaction of PVC with NaBT is carried out in different solvents or at different temperatures, the results must vary. In fact, it is known that the intensity of PVC-solvent and PVC-PVC interactions depends on the nature of the solvent, and it can be manifested in the study of T_g versus degree of conversion, both by a change in the slope, and in the number of substituted chlorine necessary to destroy the chain-chain interactions.

Figure 8 shows the evolution of T_g of the modified polymer in diethyl malonate, 2-butanone, and cyclohexanone, and in Fig. 9 those modified in dioxane, tetrahydrofuran, and aqueous suspension. It is evident from the above result that the effect of solvent on T_g is similar for the carbonyl-containing solvents, which is clearly at variance with the ether-containing solvents. PVC does not interact with water, so that the evolution of T_g of the substituted polymer in this medium approaches that of those modified in the melt. These results are in agreement with those found in the study of PVC-solvent and polymer-polymer interactions by different authors. In fact, as was manifested in the Introduction, Maddams et al. [7–10] have studied the ability of PVC to form gels in cyclohexanone, Guenet et al. [1–6] have studied the same tendency in diethyl malonate, and

Challyck et al. [11] suggested the formation of gels in the PVC-2 butanone system. In the tetrahydrofuran- and dioxane-PVC systems some kind of interaction has also been found [19]. Furthermore, Coleman et al. [29] have extensively studied specific interactions in polymers and they define PVC as a material with intermediate strength interactions. Also, the interaction parameters for butanone and other ketones are higher than for dioxane. Taking into account these considerations, not only can the high value of T_g for the PVC modified in such solvents (in regard to that of the melt) be explained, but also the difference of the T_g behavior between ketones and ether solvents (Figs. 8 and 9). The T_g measurements cannot directly demonstrate the associations on the polymer, but these results indirectly show some degree of interaction on local parts of the chain induced by the solvent. The precise nature of interactions involved in this polymer, be they dipolar, relatively weak hydrogen bonding, or a combination of both, is a subject of debate [29], but the nature of the chlorine atoms involved in the PVC interactions are those with heterotactic and/or isotactic placements, since they are the only ones eliminated during the PVC reactions.

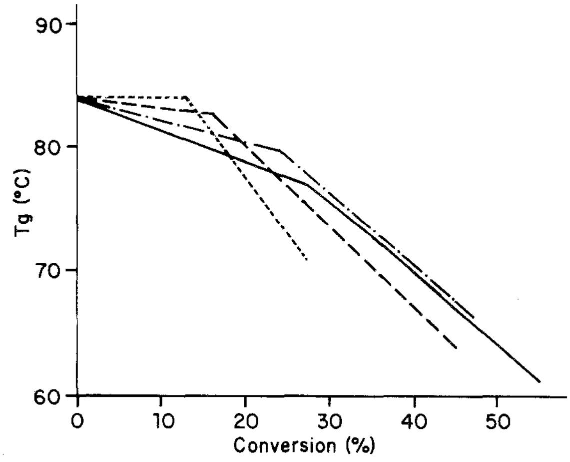

Fig. 10. Evolution of the glass transition temperature with degree of conversion for the reaction of PVC with sodium benzene thiolate in cyclohexanone at different temperatures (. . . .) 15°, (– –) 25°, (–·–) 60° and (——) 90 °C.

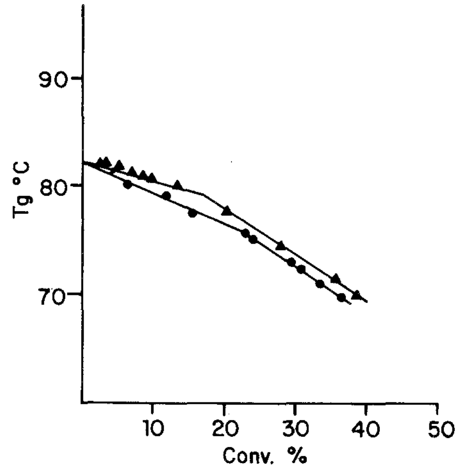

Fig. 11. Evolution of the glass transition temperature with degree of conversion for the reaction of PVC with sodium benzene thiolate in diethylmalonate at 60° (▲) and 100 °C (●)

Influence of temperature on T_g

It is also known that temperature can break or destroy gel formation of PVC in CH and DEM, as has been stated by Maddams et al. [7–10] and Guenet et al. [1–6]. Following this reasoning, in Fig. 10 the evolution of T_g with degree of conversion for the reaction of PVC with NaBT in CH at 15°, 25°, 60° and 90 °C, and in Fig. 11 the evolution of T_g for PVC modified in DEM at 60° and 100 °C are plotted. From these figures it can be said that: 1) the slope of the initial part of the plot is different for each temperature, and as the reaction temperature increases the slope moves towards that in the absence of solvent, which is in agreement with the effect of temperature destroying the gels. 2) From a certain composition, all of the plots exhibit an important change in the slope which approaches that in the absence of solvent, that is, where no interactions can take place. 3) The degree of chlorine substitution at which the interaction begins to break down vary with temperature, and the necessary degree of substitution, in the range of 15–60 °C, is lower for the lower temperature modified polymer. This third point is the opposite of what one, in principle, might expect, since in the lower temperature reactions, to obtain the same conversion takes more time, which would lead to aging of the PVC gels as stated by Maddams et al. [7–10] and Guenet et al. [1–6]. Nevertheless, the results obtained can be explained in the following way. As the reaction

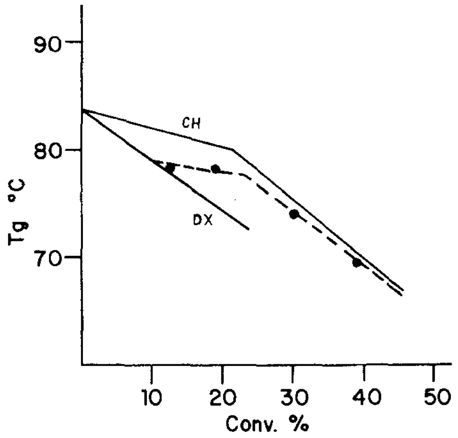

Fig. 12. Evolution of the glass transition temperature with degree of conversion for the reaction in cyclohexanone (CH) and dioxane (DX) at 60 °C. ●) Polymer modified in cyclohexanone from a 13% modified polymer in dioxane

temperature in CH decreases the interactions of PVC-PVC and PVC-solvent are higher and the polymer obtained will be more associated. For the same chemical composition a more associated (ordered) polymer gives high T_g values, but a more ordered polymer is easier to destroy than the less ordered polymer. Unfortunately, there are no studies in the literature to confirm this explanation, or giving any other interpretation. These results need to be considered separately, since they are not the objective of this work.

Additional proof

More evidence that the gels-interactions take place at "definite" chlorines of the chain is found in the following experiment. A sample of a 13% modified polymer with sodium benzene thiolate in dioxane at 60 °C was extracted and purified, then allowed to react in cyclohexanone at 60 °C for a period of time, and samples were taken at different intervals. In Fig. 12 the experimental points of this run are observed along with the evolution of the glass transition with degree of substitution for the modified polymer in cyclohexanone and dioxane at 60 °C. The evolution in this case follows the behavior of that in cyclohexanone, that is, on the one hand, the same value for the slope of the initial step is found, and on the other, the degree of substitution at which the gel is supposed to break down is the same.

The fact that the identity and the amount of chlorines involved in gel formation are of a specific nature is deduced from the next argument. If 13% of these "specific" chlorines have not been eliminated in the dioxane reaction, in the cyclohexanone reaction the interactions in the polymer (shown by the T_g) would have been observed at values of more than 25% conversion, and would have changed their intensity (slope).

Conclusion

The evolution of the glass transition temperature with degree of substitution of PVCs modified in certain solvents show a positive deviation from the supposed molar additivity up to a certain degree of substitution. This anomalous behavior can only be related with interactions, thus gel-forming-solvents lead to higher values of T_g than do polymer-light interaction-solvents.

Since only chlorines of isotactic and heterotactic triads are involved in the PVC reactions until conversion of 70% [25], gel-interactions in the PVC chain must be caused by chlorines of isotactic and/or heterotactic triads.

The substitution reaction of PVC in the above solvents only provides indirect evidence for PVC gelation. Nevertheless, this method can be of great interest in the study of the gelation mechanism of PVC proposed by Guenet et al. [1–6], if systematic studies of gel formation (by elastic and quasielastic light-scattering measurements) in PVCs of the gradual chlorine elimination were undertaken. Thus, we can correlate the aggregate size with the amount and the nature of chlorines involved in their formation. At this point, Guenet et al. [1–6] have proposed that chlorine atoms other than syndiotactic ones can be responsible for gel formation in PVC.

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