Influence of the reaction medium and the reactant on the glass transition temperature of chemically modified poly(vinyl chloride)

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Copolymers based on substituted poly(vinyl chloride) (PVC) produced by reacting PVC with different thiolates in cyclohexanone solution and in the absence of solvent (melt), show different glass transition temperatures, T_g, for the same chemical composition. The variation of T_g for the vinylchloride–vinylthiobenzene, vinylchloride–vinylthiocresol and vinylchloride–vinylthionaphthol copolymers obtained in the melt follows the Fox equation. However, the same copolymers obtained in cyclohexanone show a deviation from this trend of T_g as a function of molar composition. Factors such as microstructure, chemical composition distribution and molecular weight do not change appreciably from solution to the melt, and therefore cannot be responsible for these differences in the T_g values. We attribute the deviation in the T_g values of copolymers obtained in cyclohexanone solution to polymer–polymer interactions produced at local sites on the chain, and we propose that these interactions are related to chlorine atoms in isotactic and/or heterotactic triads.

(Keywords: glass transition temperature; poly(vinyl chloride); copolymers)

INTRODUCTION

The glass transition temperature, T_g, of copolymers was first predicted by Fox[1] based on the additive relation of the weight fractions of the two monomers. Subsequently various semiempirical equations have been proposed[2–4], giving the T_g of a copolymer in terms of the T_gs of the corresponding homopolymers. Nevertheless, many copolymers exhibit deviations in the plots of T_g *versus* composition and thus other factors such as microstructure, interactions, molecular weight and composition distribution have been taken into consideration to explain the results. Accordingly, several equations have been proposed to describe the phenomenon. The influence of sequence length distribution of comonomers has been investigated and new expressions have been derived[5–7]. These equations have been applied to several examples in the literature[8–12]. As far as poly(vinyl chloride) (PVC) is concerned, there is an example in the literature of polyethylene (PE)–PVC copolymers where the deviation in the T_g with composition is attributed to the different composition distribution[13]. Interactions in copolymers have been treated as for the case of polymer blends, and some examples have also been resolved[4,14].

The current study involves nucleophilic substitution reactions of PVC with sodium isooctyl thiosalicilate, sodium isooctyl thioglicolate and sodium benzene thiolate in different solvents, at temperatures ranging from 5 to 60°C, in both aqueous suspensions and discontinuous and continuous melts; we have demonstrated, by ^{13}C n.m.r., that the mechanism of the reaction is stereospecific. It is shown that only chlorines of isotactic and heterotactic triads are reactive[15–20].

In a very recent study[15] of the T_g of PVC copolymers, $(CH_2\text{–}CHCl)_n\text{–}(CH_2\text{–}CHSC_6H_5)_m$, obtained by the substitution of PVC with sodium benzene thiolate in different solvents, we have observed that the evolution of T_g with molar composition depends on the type of solvent. When the substitution reaction is carried out in the melt, that is, in the absence of solvent, the plot of T_g as a function of chemical composition practically coincides with the T_g predicted by the Fox theory. Nevertheless, when the reaction is carried out in the presence of gel-forming solvents, such as butanone, diethyl malonate, etc., the T_gs of the copolymers are much higher than those normally expected on the basis of chemical composition. These results suggest that the solvent promotes specific associations, aggregation or interactions at local sites on the polymers, associated with chlorines in isotactic and/or heterotactic configurations.

We consider that, to confirm the importance of the solvent, a general comparison of the above results with different reactants, and further analysis of the variation of T_g in the PVC copolymer with molar composition, are required in order to eliminate the possible influence of other effects. We have therefore chosen a group of reactants of very similar chemical nature but with increasing size, in order to study the influence of the

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reaction medium on the T_g of chemically modified PVC. We briefly discuss the study of the influence of reaction solvent on the T_g of PVC copolymers obtained by chemical substitution with sodium benzene thiolate, sodium thiocresolate and sodium thionaphtholate.

EXPERIMENTAL

Materials

The initial polymer was bulk polymerized PVC obtained from Rio Ródano Industries, Spain. The molecular weight, determined by osmometric measurements, is $M_n = 32\,000$, and the tacticity is $i = 19.6$, $h = 49.8$ and $s = 30.7$.

The reactants, sodium benzene thiolate (NaTB), sodium *p*-thiocresolate (NaTC) and sodium thionaphtholate (NaTN), were synthesized from the corresponding thiol by reaction with metallic sodium in *p*-xylene, as described elsewhere[15,21].

Cyclohexanone was obtained by double distillation of the commercial product. Tetrahydrofuran (THF) was distilled in the presence of lithium aluminium hydride.

Nucleophilic substitution reactions

Solution reaction. Solution substitution reactions were carried out in cyclohexanone at 60°C in an equimolar concentration of PVC and the reactants NaTB, NaTC and NaTN, respectively. At progressively increasing reaction intervals, samples were withdrawn, precipitated with methanol (MeOH) and purified twice with THF–MeOH as the solvent–precipitant system. The copolymers obtained were: vinylchloride–vinylthiobenzene $\text{-(}CH_2\text{–}CHCl\text{)-}_n$ $\text{-(}CH_2\text{–}CHSC_6H_5\text{)-}_m$ copolymer (VC–VTB); vinylchloride–vinylthiocresol $\text{-(}CH_2\text{–}CHCl\text{)-}_n$ $\text{-(}CH_2\text{–}CHSC_6H_4CH_3\text{)-}_m$ copolymer (VC–VTC); vinylchloride–vinylthionaphthol $\text{-(}CH_2\text{–}CHCl\text{)-}_n$ $\text{-(}CH_2\text{–}CHSC_{10}H_7\text{)-}_m$ copolymer (VC–VTN).

Melt reactions. Melt substitution reactions of PVC and the corresponding sodium thiolate were carried out in a Brabender plasticorder internal mixer coupled to a torque register. The reactions were performed in a single step with different amounts of PVC and thiolate. The processing conditions were 160°C and 40 rev min^{-1}. At appropriate reaction times, samples were withdrawn and purified three times with THF–MeOH.

Characterization

Determination of the degree of substitution. The degree of substitution of PVC samples obtained with NaTB, NaTC and NaTN, either in cyclohexanone or in the melt (expressed as mol% vinylthiolate/vinylthiolate–vinylchloride) was determined by u.v. spectroscopy using a calibration curve for each of the three reactants. The calibration curves were drawn from data for samples with a known degree of conversion obtained by elemental analysis and ^{1}H n.m.r. spectroscopy, as described elsewhere[15,16,21].

Determination of the number average molecular weight. The number average molecular weight was determined in a Knauer membrane osmometer at 34°C from polymer solutions in cyclohexanone at 34°C and at four different concentrations.

Determination of microstructure. Evolution of polymer tacticity was followed by ^{13}C n.m.r. in a Varian 300 XL spectrometer operating at 75.5 MHz and 80°C in deuterated dioxane under conditions described previously[15–18]. The resonances used were those of the methynic carbons of the backbone, ranging from 57.0 to 60.0 ppm. Information concerning ^{13}C n.m.r. signals for the substituted polymers has already been given[16,17,22]. The calculations were carried out by measuring the relative areas of the different peaks in this part of the spectrum with a compensating polar planimeter.

D.s.c. measurements. The calorimetric measurements of substituted PVC were carried out in a Perkin-Elmer DSC-4 differential scanning calorimeter, coupled to a thermal analysis data station. The d.s.c. curves were obtained at a heating rate of 10°C min^{-1} 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 d.s.c. curves measured from the extension of the pre- and post-transition base line.

RESULTS AND DISCUSSION

Results of the synthesis and characterization of the VC–VTB, VC–VTC and VC–VTN copolymers are reported separately[15,21].

The chemical nature of the three vinyl groups is identical in each case, so that no variations in T_g are expected, except those that obviously arise from the volume of reactant, such that VC–VTB < VC–VTC < VC–VTN. In *Figures 1*, *2* and *3* the changes of T_g with molar composition are represented for the three copolymers obtained by the chemical modification of PVC in cyclohexanone and in the melt, with sodium benzene thiolate, sodium thiocresolate and sodium thionaphtholate, respectively. From these figures it is seen that, as expected, the T_g of the VC–VTN copolymer is higher than that of VC–VTC, which is higher than that of the VC–VTB copolymer. However, for all the reactants, the T_g of the copolymers obtained by the reaction in

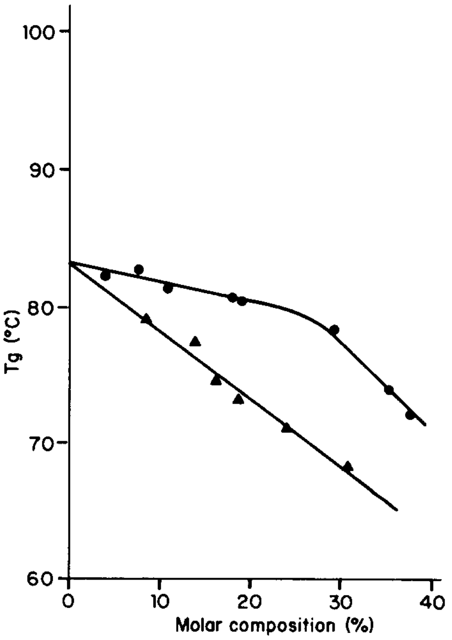

Figure 1 Variation of T_g as a function of molar composition of VC–VTB copolymer, obtained in cyclohexanone (●) and in the melt (▲)

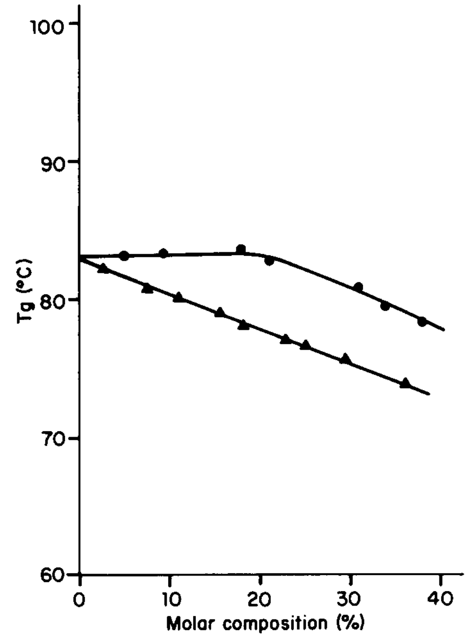

Figure 2 Variation of T_g as a function of molar composition of VC–VTC copolymer, obtained in cyclohexanone (●) and in the melt (▲)

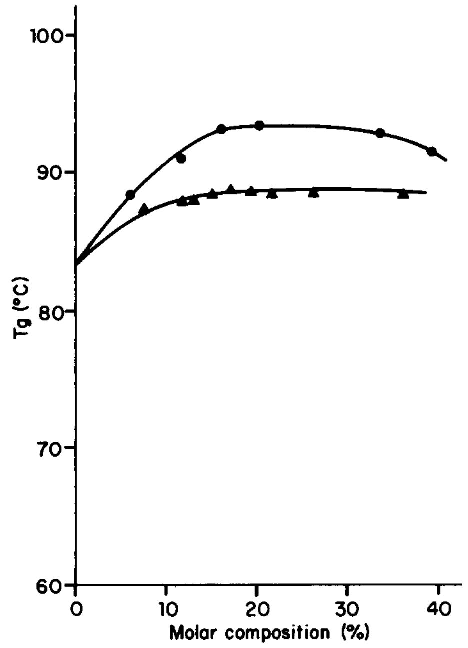

Figure 3 Variation of T_g as a function of molar composition of VC–VTN copolymer, obtained in cyclohexanone (●) and in the melt (▲)

cyclohexanone is higher than that obtained in the absence of solvent.

It was supposed that the T_g for the polymer obtained in the melt could only depend on the chemical composition, since there is no influence from the solvent. Consequently, we have represented the results in terms of the Fox equation in *Figure 4*. It can be seen that the experimental data of the copolymers fit the theoretical T_g values. The values of T_g obtained from the slopes of the three representations corresponding to poly(vinylthiobenzene), poly(vinylthiocresol) and poly(vinylthionaphthol) homopolymers are 51.8, 65.7 and 89.9°C, respectively.

For several reasons that have already been published[16], it is not possible to obtain a 100% substituted PVC, therefore we have synthesized, as an example, poly(vinylthiobenzene) by radical polymerization from vinylthiobenzene monomer. The T_g found for this polymer is 52.0°C, which is the same as that obtained from theoretically modified PVC in the melt. Accordingly, we can say that the T_g of the modified PVC with thiolate reactants in the melt can be expressed in terms of chemical composition by the Flory equation, without taking into consideration any other appreciable effect.

As the T_g values of VC–VTB, VC–VTC and VC–VTN copolymers obtained in cyclohexanone clearly show positive deviations from their supposed molar additivity, other factors must be suggested to explain the variation. In the literature, the influence of tacticity, of specific interactions and of chemical composition distribution have been recognized as the main factors that can play important roles in the determination of the T_g of copolymers. Also, the molecular weight is known to alter the T_g of the polymers. Consequently we have analysed the results in terms of the above-mentioned parameters.

Influence of molecular weight

This study is based on the fact that nucleophilic substitution could bring about side reactions, such as scission or crosslinking, both in a solvent at intermediate temperature and in the melt, at high shear rate and temperature, which could increase or decrease

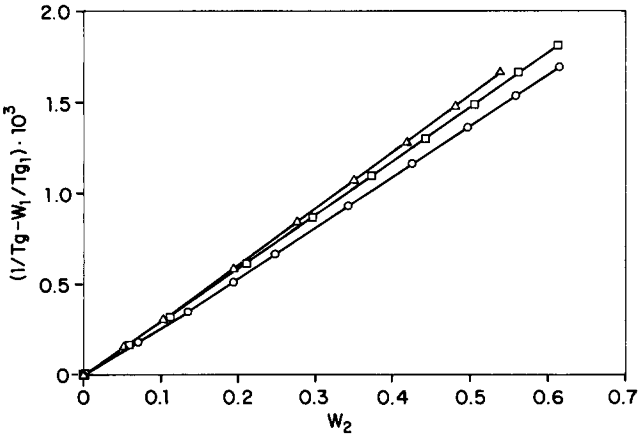

Figure 4 Comparison of the theoretical T_g values calculated from the Fox equation to the experimental T_g values of PVC copolymers obtained by melt modification: ○, VC–VTB; △, VC–VTC; □, VC–VTN

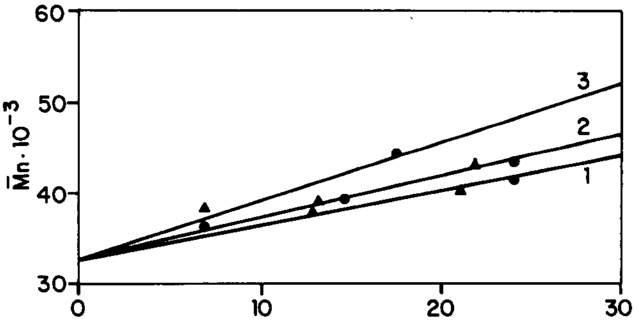

Figure 5 Dependence of number average molecular weight on molar composition of copolymers. 1, VC–VTB; 2, VC–VTC; 3, VC–VTN, obtained in cyclohexanone (●) and in the melt (▲)

the molecular weight of the polymer. Consequently, we have attempted to verify whether any minor side reactions have taken place. *Figure 5* shows the experimental number average molecular weight of the VC–VTB, VC–VTC and VC–VTN copolymers, obtained in cyclohexanone and in the melt, as a function of molar composition, together with the theoretical predictions. These results reveal that the molecular weight corresponds, both for cyclohexanone and melt substitutions, to the theoretical value, which implies that no scission or crosslinking occurs and thus the deviation in T_g is not caused by variations in molecular weight.

Chemical composition distribution

As pointed out in the Introduction, there are many examples in the literature where this parameter has a major effect on the value of T_g. In a recent similar study of the T_gs of ethylene–vinylchloride copolymers, obtained by reduction of PVC with three different reagents[13], some deviation from the calculated T_g values for random copolymers was found. The authors consider that these results are not unexpected due to the blockier structure of one of the series, and in consequence they also consider that there may be some microphase separation in the samples with high ethylene content. However, the T_g of PE is not evident in the d.s.c. thermograms.

In our ^{13}C n.m..r. study it is possible to assign exactly the position of the central sulfur triads. Nevertheless, we cannot quantify them as they are overlapped with $-CH_2-$ tetrads[15,21], and we cannot assess whether the distribution is more blocky or more random. An estimate of the difference in composition distribution in the copolymer VC–VTB obtained in cyclohexanone from that of the melt can be achieved if we compare, for the same chemical composition, the bands corresponding to the $-CH_2-CHSC_6H_5-CH_2-$ region. Up to a composition of about 20%, the spectra do not show appreciable quantitative differences. Accordingly the chemical composition should not influence the T_g. These results, reported separately[21], do not disagree with those found in ethylene–vinylchloride copolymers[13], since in the latter case the copolymers are obtained from three different reactants, and the chemical composition distribution is different in the three series because the reaction mechanism is different. In contrast, in our study each series of copolymers is obtained with the same reactant and the mechanism for the substitution reaction in the melt and in cyclohexanone has been demonstrated to be nucleophilic and stereoselective[15,20,21].

Effect of microstructure

We have already pointed out, in several published works, that the substitution reaction on PVC with different reagents, such as sodium thiobenzene, sodium isooctyl thioglicolate and sodium isooctyl thiosalicilate, in cyclohexanone, aqueous suspension and in the melt, follows a stereospecific mechanism by the reaction of the central chlorine of isotactic and heterotactic triads[15–20,22]. This stereoselective character has also been observed in the reduction reaction of PVC[13].

In *Figure 6* the variation of isotactic, heterotactic and syndiotactic unreacted chlorines is plotted against molar composition of VC–VTB, VC–VTC and VC–VTN copolymers. From this figure it can be seen that isotactic and heterotactic triads decrease linearly throughout the substitution process and syndiotactic triads apparently increase, due to the formation of a new β-substituted syndiotactic triad[17], irrespective of the reactant used or the reaction conditions. Thus, we can say that, in the reaction of PVC with NaTB, NaTC and NaTN, the same stereospecificity of the reaction and similar content of isotactic and heterotactic chlorines with degree of conversion for cyclohexanone and melt substitutions has also been found. Therefore, although it is clear that the stereoregularity has an enormous influence on the T_g, in our study it cannot explain, at triad level, the deviations in the values of T_g.

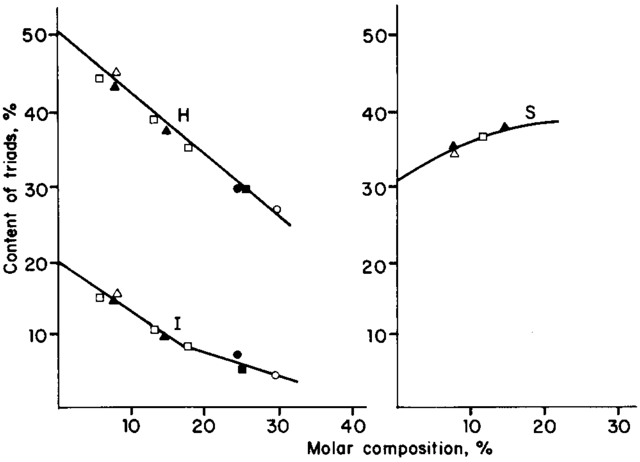

Figure 6 Variation of isotactic (I), heterotactic (H) and syndiotactic (S) triads of PVC copolymers with molar composition. VC–VTB obtained in cyclohexanone (■) and in the melt (□); VC–VTC obtained in cyclohexanone (●) and in the melt (○); VC–VTN obtained in cyclohexanone (▲) and in the melt (△)

Specific interactions

The possibility of the existence of specific interactions in the PVC and PVC–cyclohexanone systems has already been suggested by, among others, Coleman and co-workers[4,14], Jackson and co-workers[23,24] and the present authors[15,21].

In this respect, Coleman and co-workers[4,14] have extensively studied specific interactions in polymers, and they employ the criteria of weak, intermediate and strong interactions to define their strength and the ability of the polymers to self-associate. In the case of polymers with strong interactions, they derived an equation for the compositional dependence of T_g which, although initially used for miscible binary blends, is entirely applicable to copolymers containing the same type of functional groups[4]. Unfortunately, it is not clear how they should describe polymers with certain types of strongly polar functional groups, such as PVC or polyacrylonitrile[14]. There is evidence for association in mixtures involving these polymers, but it is not definitive and at present materials with intermediate strength interactions fall through the cracks in their quantitative treatment[14].

Jackson and co-workers[23,24] have studied the ability of PVC to form gels in cyclohexanone and, on the basis of Raman spectroscopic studies, have shown that gels can be associated with a definite structure consisting of consecutive syndiotactic, isotactic and syndiotactic placements.

We have already presented a third argument to explain the deviation in the T_g values in terms of specific interactions[15]. In this case we found that when PVC is modified with NaTB in gel-forming solvents, such as diethyl malonate, butanone or cyclohexanone, the T_g of the obtained copolymer only decreases clearly with chemical composition when 25% of the chlorine is eliminated. Nevertheless, in intermediate solvents, such as dioxane and tetrahydrofuran, the behaviour lies between that described above and that of the melt. As the reaction temperature increases the anomalous behaviour disappears. These results were related to PVC–PVC interactions that could gradually be destroyed by chlorine substitution and temperature, and we proposed that chlorines from isotactic and heterotactic triads were involved in the production of interactions in PVC.

In the present study we have eliminated the possibility of any other factor that could influence the value of T_g, and we have generalized the T_g studies to another series of chemically modified PVCs. All the results are in agreement with the suggestions proposed in ref. 15. This means that in all the modified PVCs in cyclohexanone there are some interactions on local parts of the chain, either self-association (Coleman and co-workers) or new interactions produced by the cyclohexanone (Jackson and co-workers), which prevent chain mobility and are therefore responsible for the high values of T_g, until a certain percentage of chlorine is eliminated by any one of the reactants. In the case of melted modified PVC it is clear that these interactions have been eliminated.

The amount of chlorine necessary to eliminate the interactions depends on the size of the incorporated group. It is obvious that the bigger the group introduced by the chemical reaction, the less will be needed to interrupt the polymer–polymer interactions. As a result, we have found values of incorporation of 25% for thiobenzene, 20% for thiocresol and 15% for thionaphthol, which correspond to the small, intermediate and large reactant size.

As Coleman *et al.*[14] point out, the precise nature of the intermolecular interactions involved between the chemical moieties of PVC, be they dipolar, relatively weak hydrogen bonding or a combination of both, is the subject of debate. Nevertheless, the chlorines involved in the PVC interaction are only those atoms with heterotactic and/or isotactic placement, as they are the only atoms eliminated by reaction of PVC with all of the reactants studied here.

These results represent a new method for the study of gel formation, interactions and aggregations in PVC by means of controlled stereospecific reactions on the polymer. It provides an easy route to the identification of the nature of chlorines involved in the above problems.

CONCLUSIONS

The variation of the T_g of PVC copolymers, obtained by chemical substitution of PVC with sodium benzene thiolate, sodium thiocresolate and sodium thionaphtholate in the absence of solvent (in the melt), with molar composition follows the Fox equation. The variation of T_g of the same copolymers obtained in cyclohexanone solution with molar composition clearly deviates from the above behaviour.

For each series of copolymers, the tacticity, chemical composition distribution and molecular weight do not change appreciably between the cyclohexanone and the melt. Therefore, we interpret the differences on the basis of polymer–polymer interactions. These interactions must be caused by chlorine atoms in isotactic and/or heterotactic triads since they are the only atoms eliminated progressively in the PVC substitution reactions.

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