Macromol. Symp. ***2001,*** *166, 25-33*

Some Consequences of the Polymer-Solvent Interaction

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SUMMARY: In this paper we report recent results concerning the consequences of polymer-solvent interactions in different areas of polymer materials. First, we discuss the effect of polymer-solvent interactions in the glass transition temperature of copolymers obtained by chemical modification of polymers in gel forming solvents. In a second part, we present the relevant role of the solvent and the polymer microstructure in the formation of physical gels. In the final part of the paper we present some recent technological applications of polymer gels.

Introduction

It is well known that the ability of a polymer to interact with a particular solvent entails important consequences in the behaviour of the polymeric systems. For instance, under specific conditions of temperature and concentration a polymer-solvent system can give rise to associations, intermolecular complexes, aggregates or physical gels1-4). These polymer-solvent superstructures present a combination of structural characteristics and properties which make them suitable for multiple technological applications5,6).

It is well known that polymer-solvent interactions in dilute and semidilute solutions also determine the physical and chemical properties of the polymer solutions. However, few studies exist about how the polymer-solvent interactions can affect the nature and properties of copolymers obtained by modification reactions of homopolymers in solution media, as well as the kinetics of the reaction.

The copolymer glass transition temperature can be predicted as a function of chain flexibility, i.e., copolymer composition, composition distribution and stereoregularity, taking into account other factors as the molecular structure or supramolecular organisation of the system7-11). The question is whether or not the solvent in which the copolymer is obtained plays a role in the final properties of the copolymer.

During the last years, a range of new studies on polymer thermoreversible gels has emerged: on the one hand investigations in the field of analysis of molecular structure and gel

CCC 1022-1360/00/$ 17.50+.50/0

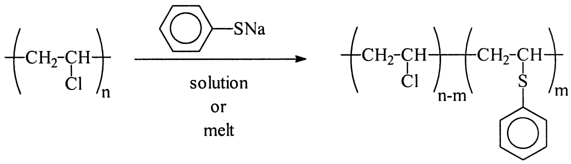
formation and, on the other, studies concerning the mechanical properties and the numerous applications of those materials[12)]. Nevertheless, until recent years, a systematic study of the influence of the polymer microstructure, the solvent type and the relations between them, has not been carried out, except for few examples[12,13)], even though polymer gels arise as a consequence of polymer-solvent interactions.

The technological applications of polymer gels make use of the elastic properties of the materials arising from a three-dimensional network[5,6)]. Gels with special properties may be obtained by the inclusion within the polymer network of components with specific properties or by the replacement of the solvent by air (aerogels)[14)] or by a reactive solvent (interpenetrating networks)[15)].

In this paper we present some examples concerning the above mentioned subjects, i.e., the influence of the polymer-solvent interactions in the glass transition of copolymers obtained by modification reactions, the influence of polymer microstructure and polymer-solvent interactions in the formation of polymer gels and the preparation of a new type of materials with defined properties.

T_g of copolymers obtained by polymer modification reaction

The glass transition temperature, T_g, of copolymers was first predicted by Fox[7)] based on additive relation of the weight fractions of the two monomers. Subsequently various semiempirical equations have been proposed, giving the T_g of a copolymer in terms of the T_gs of the corresponding homopolymers[8-11)]. Nevertheless, many copolymers exhibit deviations in the plots of T_g versus composition and thus other factors such as microstructure, molecular weight, polymer interactions 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 the sequence length distribution of comonomers, the composition distribution and the interactions in copolymers have been investigated and new expressions have been derived[16-18)].



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Furthermore, in a recent study of the T_g of PVC copolymers obtained by the substitution of PVC with sodium benzene thiolate in different solvents (see scheme 1), a new factor affecting the T_g of copolymers was found which is the reaction medium (solvent type, temperature, etc.)[19].

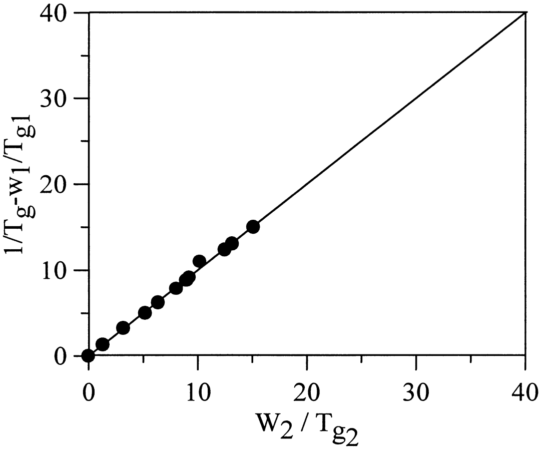


Fig. 1: Comparison of the theoretical T_g values calculated from the Fox equation (—) to the experimental T_g values of PVC copolymers obtained by melt modification (●).

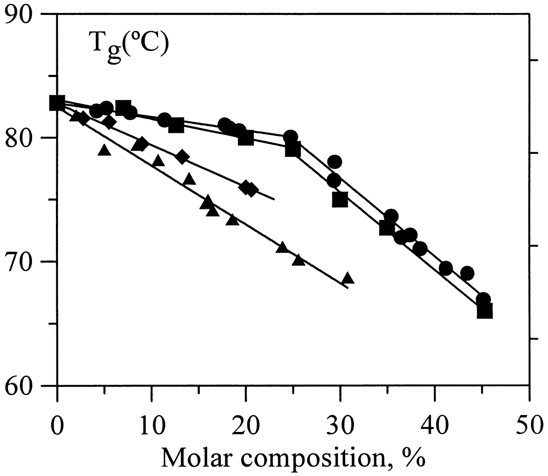
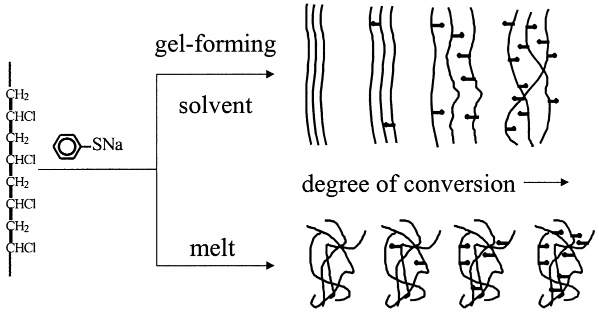


Fig. 2: Variation of T_g as a function of molar composition of copolymers obtained in cyclohexanone (●), butanone (■), dioxane (◆) and in the melt (▲).

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 (Fig. 1). However, when the reaction is carried out in the presence of gel-forming solvents such as butanone, diethyl malonate, cyclohexanone, etc., the T_gs of the copolymers are much higher than those expected on the basis of their chemical composition (Fig. 2).

The importance of the solvent was confirmed by means of additional studies of modification reactions at different temperatures and with the reactants sodium thiocresolate and sodium thionaphtolate$^{20)}$. The variation of T_g with chemical composition for each copolymer series depends on the type of solvent and the reaction temperature.

For each copolymer the tacticity, chemical composition distribution and molecular weight do not change appreciably in the different reaction media: solvents or melt. Therefore, we interpret the differences on the basis of interactions, associations or aggregations at local sites on the polymer promoted by the solvent.



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We can consider the following explanation for the variation of the T_g of copolymers obtained in different media and at different temperatures: when dissolving PVC in a gel-forming solvent such as cyclohexanone or diethyl malonate, new polymer-solvent interactions appear in the system promoting an ordered structure with a certain degree of packing (see scheme 2). At low conversions the ordered structure is not very distorted by the thiol group and therefore, the molecular motion (T_g) of these copolymers is influenced by the contributions of both, the chemical composition and the molecular structure of the polymer. As the degree of conversion increases (up to 15-25 mole %), the above structure is progressively destroyed and the contribution of the chemical composition to the T_g variation plays an increasingly important role, approaching the value of the melt. When the reaction is carried out at different temperatures, the degree of packing of PVC chains changes and the variation of T_g with molar composition approaches the value of the melt at increasing temperatures.

Thermoreversible gels

A second example of the importance of polymer-solvent interactions is the formation of polymer gels. The results and conclusions obtained in the previous section have shown that controlled stereospecific reactions on the polymer represent a new route for the study of gel formation, interactions and aggregations in PVC and other polymers. It provides, thus, an easy mean to clarify the role of the polymer microstructure in the thermoreversible gelation of polymers.

The propensity of PVC to form thermoreversible gels with a variety of organic solvents has been known for over 50 years. The reason why such poorly-crystalline polymer should give strong gels has always been a matter of debate. Recently, a fibrillar model based on the formation of a polymer-solvent complex has been proposed by Guenet12). Nevertheless, there is not a single model explaining all, the formation, the molecular structure and the viscoelastic properties of PVC gels. In this sense, there are few works dealing with the influence of polymer microstructure and solvent type.

Thus, it was necessary to study systematically the role of the polymer microstructure, where the chlorine atoms participating in the formation of the polymer-solvent complex were identified, localised and quantified. In this sense attempts were made to prepare model compounds of PVC with variable content of chlorine atoms by chlorination of PE and PVC21,22). Yet, the radical character of the reaction made it difficult to obtain controllable structures. Another route involved the preparation of highly crystalline PVC by polymerization and its effect in gel formation23).

Our approach to study the influence of the PVC microstructure and solvent type in the formation of gels was the preparation of model compounds of PVC with variable content of chlorine atoms by substitution reactions24-25). The correlation of the molecular structure and the viscoelastic properties of the gels prepared from these model compounds in different solvents with the polymer microstructure allowed us to establish a cause-effect relation in the gelation of PVC assuming that the origin is the polymer-solvent interaction.

Model compounds of PVC. By chemical modification of PVC we obtained two series of copolymers of general formula $-(CH_2\text{-}CHCl)_m-(CH_2\text{-}CHX)_n$ where X=-H (series EPVC) and X=-SC_6H_5 (series SPVC), respectively, and n ranging from 0 to the desired percentage of modification25). The characterisation of these copolymers leads to the following conclusions:

i) the chain length of the copolymers is the same than that of the original PVC, ii) random copolymers are obtained and iii) chlorine substitution occurs only on the isotactic and heterotactic triads. These results allow us to consider these copolymers as homologous series of PVC. When n is small enough, the behaviour of any copolymer is representative for the PVC behaviour in which n chlorine atoms (isotactic or heterotactic) are randomly eliminated from the PVC chain.

Molecular structure of PVC gels. By SANS experiments carried out from these model compounds of PVC in diester solvents (DEO, DBO), it was observed that small modifications of the polymer microstructure of the solvent type significantly alter the gel structure26). As an example, the molecular density of the fibrils which constitute the structure of the gel decrease rapidly with the elimination of isotactic and heterotactic chlorines. This result allows us to correlate the elimination of additional interactions in the system with the suppression of these types of chlorines26).

Viscoelatic properties of PVC gels. The elastic modulus of the gels prepared from the model compounds of PVC gradually decreases as the number of chlorine atoms decreases27). The analysis of the dependence of the elastic modulus with polymer concentration for all polymers in diester solvents, using different elasticity theories, showed an enthalpic origin for the elasticity of PVC gels. This elasticity behaviour changes from enthalpic to entropic (see Table 1), as the isotactic and heterotactic chlorines are eliminated. This finding is in agreement with the results obtained from SANS measurements, that is, with a rigid fibre-like structure formed by weak PVC-solvent weak links using isotactic and heterotactic chlorines28).

Table 1. Fractal dimension (1/ν, Jones and Marques theory) and non-ideal parameter (a, Clarck and Ross-Murphy theory) for gels of the series SPVC and HPVC in diethyl oxalate (DEO) and dibuthyl oxalate (DBO).

Composition (mole %)	DEO				DBO			
	SPVC		HPVC		SPVC		HPVC	
	1/ν	a	1/ν	a	1/ν	a	1/ν	a
0	1	6.7	1	6.7	1.8	4.7	1.8	4.7
3	1.5	2.5	1.2	7.5	1.8	1.8	1.8	4.5
10	1.9	1.3	1.3	6.5	1.9	1.5	1.6	4.5

Polymer-solvent complex. The role of the polymer-solvent interactions in the formation of PVC gels was studied by high resolution ^{1}H-NMR spectroscopy[29)]. The existence of such polymer-solvent complexes was demonstrated and correlated to the decrease of the values of the elastic modulus and the molecular density of the fibres, with the disappearance of isotactic and heterotactic chlorines.

As stated above, the body of experimental data suggests that there is a straight relation between molecular structure and viscoelastic properties of PVC gels and the polymer microstructure and solvent type. We can conclude that the origin of the high modulus values and the compact structure of PVC gels resides in the establishment of polymer-solvent interactions in the less stereoregular parts of the polymer.

Technological applications of polymer gels

Softness, elasticity, and the capacity to store a fluid make gels unique materials. Technological use of thermoreversible gels is widespread, including the textile, paper, packaging, cosmetic, health care (including the pharmaceutical sector), oil field, photographic and food industries. More recent interest has been shown in thermoreversible gels as examples of smart materials for switches, actuators and sensors. The photographic industry, in particular, has after 100 years, still not found a better material than gelatin for the film emulsion base[5-6)].

Thermoreversible gels are leading to more and more industrial developments, especially when materials with special properties are sought. As an example, it has been recently reported in the literature the preparation of semi-interpenetrating (SIPN) polymer networks[15)] or the preparation of magnetic gels for high density magnetic recording applications[30-32)].

SIPN are a kind of materials made up to improve the properties of one of their constituents: processing properties, stiffness, stability against phase separation, etc. Nevertheless, this type of polymer networks is not easy to obtain and to purify. As reported recently[15)], in the case of SIPN from PVC and a thermosetting polymer the difficulties are avoided due to the polymer-monomer interactions occurring in a medium in which the solvent acts as a gel forming solvent and a monomer for thermosetting.

Besides the originality, interpenetrating chemical (polyepoxide) and physical (PVC) gels can be expected to exhibit very specific and attractive properties. For instance, these materials may constitute an interesting alternative to increase the fracture toughness of polyepoxide networks. Another potencial application is to use the thermoreversibility of a physical gel to control the initial viscosity and processability of coating formulations. The concept of interpenetrating chemical and physical gels may also be extended to other semicrystalline thermoplastics (PVDF, syndiotactic PS) able to form physical gels in solution, provided the appropriate reactive solvents are found15).

Novel polymer gels that are responsive to external stimuli have been developed in the past years. The stimuli including temperature, pH, solvent, electric field, light intensity as well as the introduction of specific ions has been demonstrated to induce discontinuous volume changes5,6). A new type of magnetoelastic or magnetostrictive material has been developed by introducing finely distributed colloidal particles, having superparamagnetic behaviour into a polymer gel. The resultant magnetic field sensitive gel, called ferrogel, exhibits significant shape distortion in a nonuniform magnetic field due to the coupling of magnetic and elastic properties33).

Potential applications exist for ferrogels in information storage (high density recording media), generators, electronic circuitry, sensors and electrical tranformers30-32).

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