Structural and Entropic Effects of Blending Polymers with Liquids

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ABSTRACT: The absence of spontaneous blending of an amorphous polymer with a liquid, when their solubility parameters coincide, is explained by a specific feature of the polymer supermolecular skeleton. The process of spontaneous blending requires dissolving the supermolecular skeleton and takes place only under the sufficient entropy−donor activity of the liquid. The lack of this activity rules out the spontaneous process. However, the compatibility does occur *via* indirect pathway when stimulating a proper excitation or disintegration of a supermolecular carcass. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1693–1700, 1998

Key words: carcass sponge micelle; liquid; miscibility

INTRODUCTION

Numerous experimental and theoretical investigations make the efforts to bring any brightness relative to the structure of polymers being called amorphous ones so far. This paper presents new data which are in touch with the structural problem as well as a new approach to the morphologic description and analysis of the polymer matrix. The supermolecular organization of noncrystalline polymers is thought to be formed as a carcass body whose cells are stabilized to form the polymer chain sponge micellae completed with micropores, which are more or less narrow in sizes.

The prehistory of the carcass-micelle assembling of the polymer body affects the occuring interzone force balance as well as thermodynamic affinity of the polymer relative to low molecular liquids. As a result, the solubility parameters ascribed to polymers due to the techniques known in literature are often in failure.

The coincidence of the solubility parameters (δ) for various liquids is known to ensure their compatibility. The process results due to an increase in entropy.[1,2] However, an agreement between the δ values for an amorphous polymer and a liquid does not result necessarily in spontaneous blending. This disagreement has no certain explanation when assuming the amorphous polymer to be a high-viscosity liquid.

Up to the present, it was believed that only transient structural elements exist in noncrystalline polymers. These elements are thought to be in the fluctuation process of their generation, rearrangement, and decay.[3] However, the increasing amount of experiments points to the permanent supermolecular organization in noncrystalline polymers. As shown in this article, the supermolecular structure is responsible for the compatibility to be or not to be in perfect fulfillment. It is shown that even spontaneous mixing is rather poor; the blend is prepared by destructuring the polymer matrix under the common solvent.

EXPERIMENTAL

Cellulose triacetate [CTA; acetate number = 62.5%, M_v = 330,000, δ = 19.0 (J cm^{-3})$^{0.5}$], poly-

(methyl methacrylate) [PMMA; M_n = 140,000, δ = 19.0 (J cm^{-3})$^{0.5}$], and polycarbonate [PC; "Macrolon," M_v = 25,500, δ = 19.5 (J cm^{-3})$^{0.5}$] were used to blend with the known plasticizer, liquid dibutyl phthalate [DBP; boiling point = 340°C, δ = 19.3 (J cm^{-3})$^{0.5}$].[4] According to the general idea,[1,2] the previously described polymers should be spontaneously compatible with DBP. However, the glassy films, prepared from solutions of these polymers in methylene chloride [MC; boiling point = 40°C, δ = 19.8 (J cm^{-3})$^{0.5}$],[5] showed no evidence of dissolving in DBP, as well as noticeable swelling.

RESULTS AND DISCUSSION

The Effect of Blend Pathways

Thin PMMA and PC films experience brittlelike breaks into isolated pieces under liquid DBP in 24 h, breaking itself in DBP in minutes at elevated temperatures (60°C for PMMA and 95°C for PC films), but remaining in the glass state. On the contrary, all of the polymers become sticky immediately when contacting with MC.

To accelerate blending, granules of commercial PMMA (2 mm in sizes; methyl methacrylate (MMA) content: 3–4%) were heated at nearly 100°C (the deglassifying region) in DBP for several hours. Nevertheless, the granules cooled down to room temperature and showed no stickiness. Heating of the DBP-containing PMMA films in DBP at 60°C (to accelerate the relaxation processes and to get the value of T_g = 30°C, 30 wt % of DBP was introduced in PMMA[4] through MC) results in their fast disintegration into pieces, preserving the glassy state at room temperature for months until complete evaporation of the DBP liquid layer.

Although these polymers do not dissolve spontaneously in DBP, these make the blends in a variety of ratios through a common solution in a proper volatile solvent. Thus, according to differential scanning calorimetry (DSC) measurements, blends composed from PMMA and DBP *via* a solution in toluene are completely compatible up to a ratio of components of 1 : 1.[4] We prepared DBP-containing polymer films through solutions in MC by evaporating the solvent in a glass Petri dish covered with a glass plate. Samples with DBP content of up to 30% in PMMA and PC, and up to 86% in CTA were prepared for experiments. All of the films were transparent, did not show stickiness inherent in mixtures of the polymers
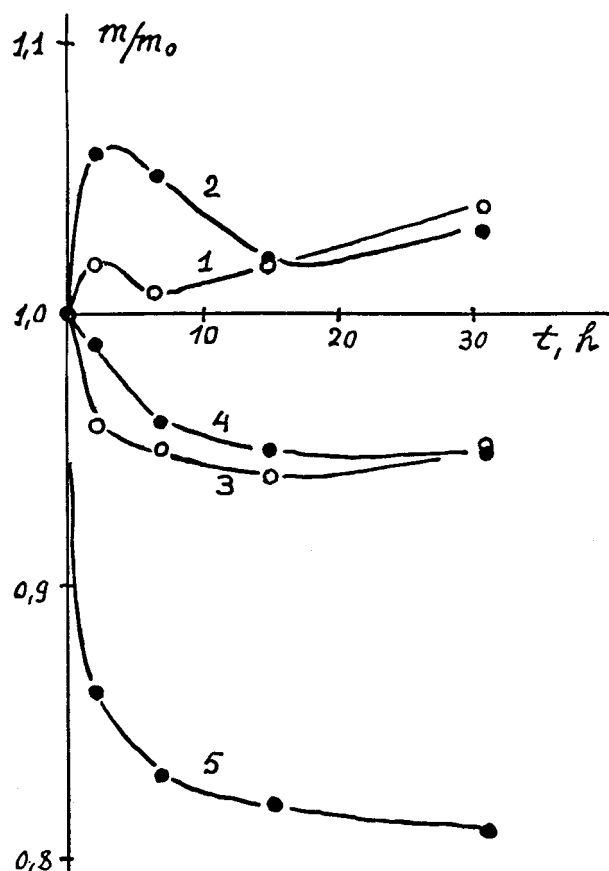
Figure 1 The relative mass response for CTA patterns when heated in DBP medium at a temperature of 98°C. The concentration of DBP in polymer is shown: 0 (1), 19 (2), 43 (3), 65 (4), and 86 mass % (5).

with MC, and exhibited no indication of dissolution in liquid DBP for many days.

Figure 1 shows the curves for the relative mass m/m_o change of the CTA–DBP blend films (30–40 μm in thickness) when heating the films under liquid DBP at 98°C. (The residual DBP layer was removed from the films with filter paper before weighing.) The change in the m/m_o parameter is practically completed within 30 h. An insignificant increase of this value (by 3–4%) for the samples containing 0 and 19% of DBP (curves 1 and 2, respectively) seems to result from DBP penetration and adsorption onto surfaces of internal structural voids. The samples with 43, 65, and 85% DBP lose up to 5% (curves 3 and 4) and 19% (curve 5) in weight, respectively, eliminating DBP from the films. So, DBP content in the respective films is reduced to 40, 61, and 70%. The initial mass of the polymer remains constant, as evidenced by weighing the films after complete

extraction of the residual DBP by heptane at 98°C [for heptane: $\delta = 15.36$ (J cm^{-3})$^{0.5}$; see ref. 5].

These results are important. They cannot be interpreted assuming that the system has not equilibrated yet, since the relaxation process is slow. Nor dissolving neither swelling of the films is observed at room temperature or at the condition of 98°C when the plasticization and high-temperature factors superimpose toward the most enhanced molecular mobility. According to the curves in Figure 1, the structural–mechanical equilibrium of the film–liquid system is accomplished within 30 h. The absence of dissolving and swelling of the films is indicated by the equilibrium amount of DBP blended.

The previously described results seem paradoxical. Indeed, the polymer and the liquid, having the identical δ parameters, are compatible when mixed in a common solvent that then is evaporated. So, one may assume that the chemical potential of DBP decreases in the polymer matter, and there is the driving force for both components to be blended spontaneously upon direct contact. But, the polymer films do not dissolve or swell in large excess of liquid DBP, despite the high DBP-blended contents and the high temperature. It is noteworthy that the films possessing the blended DBP, as previously described, 50% are related to the gel-like state,[2,6] but are compatible with an additional amount of DBP only when using the intermediate stage of dissolution of components in MC.

Structural Probing of the Supermolecular Carcass of Polymer–Liquid Blends

The absence of CTA film swelling in liquid DBP was confirmed by the diffusion probe technique using as a probe naphthalene introduced in the films from MC solutions. The rate and coefficients of naphthalene diffusion from the films were determined by measuring the optical density at $\nu = 36{,}400$ cm^{-1}. Plots of the well-known relationship $(1 - D/D_o) = (4/L)(D_d t/\pi)^{0.5}$, actually in the range of $(D/D_o) < 0.5$, were used in the case. Here, D_o and D are the initial and current optical densities, respectively; D_d is the diffusion coefficient; L is the film thickness; and t is time. Heating the films containing 1.4% of naphthalene in liquid DBP at 99°C did not result in a marked naphthalene loss within 10 h (this loss attained 13% in air with $D_d = 6.8 \times 10^{-13}$ cm^2 s^{-1}).

At the initial naphthalene concentration of 5%, its diffusivity in air is linear with DBP concentration, which is introduced in combination with naphthalene: $D_d = (0.7 \times 10^{-12} + 1.4 \times 10^{-11}$ $C_{DBP})$, cm^2 s^{-1}. Consequently, the plasticizer enhances considerably the diffusion process in films. Meanwhile, heating the films containing 5% naphthalene and 5% DBP showed about equal values of the diffusivity in air and liquid DBP [$(0.75 - 1.00) \times 10^{-11}$ cm^2 s^{-1}], indicating that an increase in the diffusion rate is not affected by DBP penetration into the film from the liquid phase.

The lack of spontaneous mixing of liquid DBP and CTA, PC, and PMMA polymers (whose solubility parameters are equal to δ of DBP) suggests a similar nature of the supermolecular organization in these polymers. Specificity is that the supermolecular structure must rigidly resist to equalization of the DBP chemical potential through the dissolution or swelling of polymers, whatever flexibility and measure of expansion of chain packing. Even gel-like films of CTA (the linear-chain polymer) containing a great amount of DBP behave relative to liquid DBP, as do the films with a completely crosslinked molecular network, differing substantially in such behavior from type 1 gel.[2,6]

Type 1 gels are thought to be composed on the base of the polymer chain network when forming the sparse crosslinks by either chemical bonds or insoluble crystallinelike domains.[2,6] These gels are characterized by the pronounced reversibility of swelling. Our system does not show such behavior, thereby indicating that they possess the crystalline bundles [paracrystalline (p) domains[7]], which not only are insoluble in DBP, but also exist being stuck to each other to produce an open-work mosaic space carcass. During formation, the p-carcass should isolate large amounts of DBP entrapped in the cells. Once the p-carcass is formed, it should exclude both dissolution and swelling of the samples in liquid DBP.

The supermolecular p-carcass should present only a small fraction of polymer chain links being arranged in the p-domain. The domains are coordinated to form the space p-carcass and simultaneously the spherical-shaped capsules enclosing the volumes of the carcass cells. The long branches of the polymer chains that are out-going from the p-domains form the grains of spongy micelles in the volumes of the p-carcass cells.

In this connection, the total change in the Gibbs energy on dissolution of such a polymer body should be the sum of two parts:

$$\Delta G^m = \Delta G_p^m + \Delta G_s^m$$
$$= \Delta H_p^m - T\Delta S_p^m + \Delta H_s^m - T\Delta S_s^m. \quad (1)$$

Here, the p and s indexes refer, respectively, to the space continuous p-carcass and the spongelike micellar grains.

According to eq. (1), MC as a solvent ensures significant contribution of the entropic terms, $[T\Sigma(\Delta S_i^m) > (\Delta H_p^m + \Delta H_s^m)]$, thus causing dispersion of the common supermolecular framework into a molecular solution. On the other hand, the entropic factor for the polymer–liquid DBP interaction prevents dissolving and swelling processes because the p-carcass seems to be rather stable to the DBP action.

Despite the failure of direct blending of liquid DBP with the polymers, there is a blend "detour" when using the common solvent capable of volatilizing. This solvent acts as a high-entropy donor in disintegrating the polymer carcass structure and then, being evaporated in the course of film preparation, transmits $\sqrt{}$ the created entropic supply to the dissolved DBP (or to another dissolved component that plays the role of the entropic acceptor). The process of the entropy-accepting is closely connected with formation of rigid supermolecular elements (p-domains), which are stable, mobile, and capable of cooperating in the form of the open-work p-carcass. These rigid domains are indicated in polymer melts and solutions by the nuclear magnetic resonance (NMR) and electron spin resonance (ESR) methods in a variety of publications. In particular, the ESR study of labeled PMMA and polystyrene (PS) (nitroxide was attached to the polymer backbone) showed those existences, even at the high solvent content of 75% and 40%, respectively, for solutions of PMMA in chloroform and PS in benzene.[8] These solutions gelatinize at room temperature, retaining up to 20–30% of the solvent in the structural-bonded state.[8] So, in the gel formed, the matrix inside every p-carcass cell should be considered a swollen sponge that possesses a high entropy related to the rest of the solvent gelatinized. The molecules of DBP occupy the places being freed of the evaporated solvent molecules in the sponge zones.

Obviously, the solvent exchange amounts to the phase transition. The following conditions apply to the process by a quasiequilibrium pathway:

$$\Delta G_g^{p,L} = 0, \quad \Delta G_p^{p,L} = 0, \quad \Delta G_s^{p,L} = 0$$

and

$$\Delta G_s^{p,L} = G_s^p - G_s^L = (H_s^p - TS_s^p)$$
$$- (H_s^L - TS_s^L) = 0$$

where the g index refers to the $\sqrt{}$ carcass of a gel, and the upper p and L indexes characterize the terms, connected with the plasticizer (DBP) and the solvent (MC), respectively. Hence, we arrive at the expression:

$$\Delta H_s^{p,L} = H_s^p - H_s^L = (TS_s^p - TS_s^L) = T\Delta S_s^{p,L}$$

wherein the change in enthalpy, $\Delta H_s^{p,L}$, has the negative sign, because the polymer does not dissolve in any amount of the plasticizer, so that the unequality $TS_s^p < TS_s^L$ is always fulfilled.

In addition, in the absence of specific interactions and, therefore, with the internal energy constant $\Delta U_s = U_s^p - U_s^L = 0$, we obtain the relationship:

$$\Delta H_s^{p,L} = U_s^p + PV_s^{\,p} - U_s^L - PV_s^{\,L}$$
$$= P(V_s^{\,p} - V_s^{\,L}) = P\Delta V_s^{\,p,L} < 0.$$

Analogous relationships $\Delta G_p^{p,L} = 0$, $\Delta H_p^{p,L} < 0$, and $\Delta V_p^{\,p,L} < 0$ characterize the process of repacking p-domains as the solvent is changed for the plasticizer.

Thus, the carcass-sponge system saturated by a nonsolvent should condense, forming ordered domain and chain-spongy zones. Consequently, the $\sqrt{}$ p-domains are tightened more closely to form the shells that are less permeably by DBP molecules. If MC displaying the entropic-donor activity is evaporated until its residue is equal to 1–2%, then the loss in the DBP amount, which is enclosed in CTA films, is 30% only in keeping the films for 1 year, even with the DBP initial content as high as 86%.

The matrix compacted $\sqrt{}$ and ordered due to a solvent change precludes swelling of CTA films in liquid DBP, even at an elevated temperature (98°C). The degree of equilibrium swelling attained by macromolecular spatial networks in a liquid, which is a nonsolvent of non-crosslinked macromolecules, is known to increase as temperature rises.[6] However, a marked loss in the plasticizer from gel-like films is observed (Fig. 1, curves 3–5). This seems to be connected to the difference in the coefficients of heat expansion for sponge zones and continuous skeleton of strongly bonded p-domains. The latter restricts the swollen sponge

expansion and creates the $\sqrt{}$ conditions $\sqrt{}$ favoring partial DBP removal.

Clearly, the previously described way of blending is realized not only for DBP, but also for other nonsolvents ("entropy acceptor"), including crystalline ones. Restrictions arise only when the enthalpic factor of the replacement in the sponge system is opposed by a great change in enthalpy, ΔH_{ph}, of the admixture phase formation $\Delta H_{ph} \leq (\Delta H_p^{p,L} + \Delta H_s^{p,L})$. In such a case, solvent evaporation gives rise to liquid or crystalline extraneous ingredients in a film.

A nonsolvent that is compatible with a polymer in an indirect way can be replaced by another nonsolvent without qualitative changing the supermolecular structure of the sample. This was revealed when using $\sqrt{}$ the CTA samples heated in liquid heptane and water at 95°C. The diffusivity of DBP, determined by its optical density at a maximum of the absorption band ($36,600$ cm^{-1}), was $\sqrt{}$ obtained in a manner like that for naphthalene. When heating in air, films containing 1.4% of DBP reveal no loss of DBP for 50 h. The desorption in air is more pronounced at 19% of DBP ($D_d = 7.5 \times 10^{-13}$ cm^2 s^{-1}). About the same D_d value is obtained for DBP diffusion in heptane from the films containing 1.4% of the placticizer, its loss being relatively low for 50 h. However, at the DBP content of 14.0%, its diffusivity in heptane increases considerably up to the value of 8.7×10^{-11} cm^2 s^{-1}. When DBP content exceeds 50.0%, the films become completely DBP-free within 1.5 h.

DBP displacement by water is characterized by the relatively high D_d value [$(2 \pm 1) \times 10^{-11}$ cm^2 s^{-1}], which is kept constant over the DBP concentration range from 1.5 to 55.0%.

As seen, heptane and water squeeze DBP out the films, with the great rate concerning the DBP desorption in air, although both liquids are poorly absorbed by the polymer and differ in their polarity and in the δ parameters. The different structural-dynamic mechanisms take place in these processes, as evidenced by the diffusivity values and in their effects on polymer films. Thus, the DBP exchange (at its initial content of 50%) by heptane is completed within 1.5 h and does not change $\sqrt{}$ film thickness (35 μm). Under water, DBP is squeezed out of the films to decrease the thickness by factors of 2–3, and the process lasts for 30 h. Obviously, in both processes, the supermolecular carcass of the polymer experiences action of mechanical forces that are different in magnitude and directionality.

Heptane is very compatible with the films that are highly plasticized, and also produces some osmotic pressure that is capable of sustaining the swelling degree and a level of segmental mobility that allows DBP molecules to escape from the carcass cells. Upon process completion, dry CTA films hold their initial thickness. This result indicates stabilization of the packless sponge micelles preserving a higher degree of emptiness due to the spatial p-carcass formed. This structural state resembles that of microporous adsorbents. In this connection, we mention that pulse NMR studies have showed that the plasticized polymers actually possess the structure typical for microporous adsorbents.[9]

Unlike heptane, water reforms CTA gels containing DBP into dense films when squeezing DBP out. This process is thought to be associated with clustering of water molecules in the sponge matrix of hydrophobic polymers.[10] The intermolecular forces inherent to water cluster in the matrix cause the hydrophobic chain links to arrange the walls of the fluctuating gaps.[11] Forming and disordering of the fluctuation gaps are accompanied by fluctuation of the water layers and drops. This process reduces the entropy excess in the system, thus inducing the process of DBP loss and stimulating work for the matrix to be compressed.

Note an interesting example when a nonsolvent is substituted by another one in PC films.[12] The films were prepared from MC solutions containing various amounts of the aromatic compound, stilbene (melting point = 124°C), and then were placed in vapors of another aromatic compound, benzophenone, at 30°C. After some months exposure to benzophenone, stilbene was completely displaced from the films. In the same samples, the amount of absorbed benzophenone was higher, with the initial amount of stilbene. The obtained result indicates that the entropy excess, preserved in the PC films due to exchange of MC by stilbene, is responsible for promoting benzophenone absorbability.

Some other ways of blending polymers with nonsolvents are known. Thus, styrene polymerization in common solutions with pentane, heptane, and octane is used to produce the transparent grains of glassy PS capable of foaming due to occlusion of volatile hydrocarbons.[13,14] Similar glasses are obtained in glassifying the PC melt under a high pressure of cyclohexane vapors.[15]

Structural Effects of the Polymer Gel-Glass Transition

The carcass-micellar effects of the blending influence the technology and using regions of the polymer blends. As known, the polymer solution is in wide practical use. The phenomenon of plasticization is of great importance for the improvement of polymer mechanical properties. Other practical fields of use of polymer blends with nonsolvent are also known. For instance, there is production of the foaming blends previously described. The polymer glasses possessing the color response are also in range.

The procedure of MMA polymerization in the presence of a great quantity of plasticizer was proposed for producing light-protective, self-bleaching PMMA glasses (containing photochromic additives) that exhibit a fast-restoring optical transparency. With the use of plasticizer, the restoring rate attains the value that is inherent in liquid solutions, although the polymer body is in the glassy state.[16] This combination of seemingly opposing properties results in entropy storing under the plasticizer accumulation inside the chain sponge zones, which are encapsulated in cells of the rigid p-carcass.

The importance of the entropic factor in the formation of carcass-assembled structures is clearly indicated in chemical crosslinking of macromolecules in solutions. For example, PS-based microporous adsorbents, exhibiting a high degree of swelling in nonsolvents, can be prepared by adjusting the rate of chain crosslinking relative to that of the relaxation of the supermolecular skeleton assembling.[17]

It is significant that polymer chains tie the p- and s-domains (so that links of certain chains fit into both of these elements of unified carcass) rather than form a mechanical mixture of particles with diverse structure. Ordering a part of the links in the domains of p-carcass creates structure-providing mechanical obstacles for ordering other links of the same chains inside the sponge s-zones.

In accordance with the aforementioned consideration, the thermodynamic equilibrium actual for the unified skeleton body formed from a solution $\sqrt{} \ \Delta G_g = \Delta G_p + \Delta G_s = 0 \ \sqrt{}$ should have the form such that the negative term $\sqrt{} \ \Delta G_p = \Delta H_p - T\Delta S_p$ (that is responsible for the stability $\sqrt{}$ of a whole supermolecular construction due to the crystal-like nature of the p-carcass) is opposed by the positive term $\Delta G_s = \Delta H_s - T\Delta S_s$ (that is

responsible for the stop in the spontaneous structurization of a system, yielding a gel instead a crystal body). Hence, it follows that the factor

$$-\Delta S_s = (\Delta G_s - \Delta H_s)/T$$
$$= (-\Delta G_p - \Delta H_s)/T > 0, \quad (2)$$

characterizing the sponge s-zones, corresponds to a decrease in entropy of the polymer-chain sponge in the gel relative to a liquid solution. The loss in entropy can reach a considerable value because the chemical crosslinking of the chains increases the cohesion energy in s-zones and between p-domains; therefore, the negative values of the ΔG_p, ΔH_p, and ΔH_s potentials.

In other words, crosslinking of macromolecules in a solution decreases the polymer compatibility with a solvent, and the latter starts approximating a nonsolvent. Simultaneously, the elastic tension of polymer chains between p- and s-zones is enhanced, with this tension being stabilized in a gel structure through intrazonal processes of ordering and crosslinking the chain links.

On transition of the crosslinked swelled gel to the dry state (the microporous xerogel is the product of drying), the solvent loss provides an amount of emptiness in the reformed sponge s-zones. This structural state is preserved by the p-carcass reformed to fix the elastic tension of polymer s-chains working under a higher load. Respectively, the term ΔG_s^d in the equilibrium condition expression of type 2, characterizing the carcass system after the drying is over:

$$-\Delta S_s^d = (\Delta G_s^d - \Delta H_s^d)/T > 0,$$

attains the substantial value to determine the entropy decrease in the sponge zones of the xerogel. At the same time, the minimum specific interaction between macromolecules and a solvent provides that the ΔH_s^d term should be insignificant with a negative sign because of a certain thickening of chain packing in the sponge matrix. Yet, evaporation of a solvent from the crosslinked gel initially possessing the swelled sponge zones does result in a considerable decrease of entropy due to a high value of ΔG_s^d equal to the work of elastic tension of s-chains.

A similar change in entropy should accompany the formation of the so-called aerogels on sublimation of a solvent from frozen polymer solutions (studied in ref. 18). The considerable value of the positive term of ΔG_s^d, attained by transiting from

a polymer solution to aerogel through the inter-mediate frozen state at a low temperature of the skeleton assemblage, increases a negative change in entropy of chain sponge of aerogel formed.

Note, the positive addition in the term ΔG_s^d for the previously described processes results from the spontaneous process of evaporation of a sol-vent. This evaporation proceeds under entropy control, with a great entropy increase, and also provides an added driving force in the work of storing elastic energy in the sponge matrix.

The dry xerogels and aerogels [being the micro-porous bodies, because the crosslinked PS pos-sessed the developed inner surface of 1,000 m^2 (see refs. 17 and 18)] attain the entropy benefit to be swelled in an ordinary nonsolvent. Actually, the entropy change region expands for the positive sign in this case. In other words, these special modes of the supermolecular assemblage, using a crosslinking of polymer chains and sublimation of a frozen solvent to include the negative entropy change in the sponge zones, promote the blending following a nonsolvent as a result of storing the structural memory in dry systems. This memory may be realized (for enough sparsely crosslinked polymers) as a considerable swelling, even in non-solvents such as water and alcohols.[17]

Because structural matrix is dilated and en-tropy is reduced, dry aerogels are unstable in thermal aging and are thickened to form the usual polymer glasses when heated.[19] Thickening also occurs when a solvent is evaporated from a non-frozen gel and, as previous described, under the water action on DBP-containing CTA gels. Note that spontaneously thickening a skeleton gel does not result in complete collapse of polymer chains inside s-zones, because the p-carcass resists this process. As a result of force-balancing both skele-ton structures under a variety of conditions for solvent evaporation, property variations of the polymer glasses appear. Indeed, the specific fea-tures of a particular physical interaction and the rate ratios of the relaxation processes at the thick-ening stage are often coupled with the prominent effects pointing to the structural memory of the glasses formed.[20,21]

Although a glass differs sharply in its physical properties from a gel, the former is the terminal product of thickening, and its structure fits in a qualitative sense a maximum dense gel. Thus, the electron microscopic study shows that the pattern of contacting grains of sizes 10–50 nm is the same for amorphous polymers, including CTA, PMMA,

and PC.[16,22–24] [Microporous gels with crosslinked chains ("polysorbs") comprise more large-sized (70 nm) globules.[25] Moreover, the electron micro-scopic examination of thin PMMA films (no more than 10 nm in thickness) allows one to prove the existence of paracrystalline domains of sizes 1.5–3.0 nm.[26]

As previously described, the skeleton structure fixed by p-domains prevents the chains from com-plete collapse in a glassy polymer. This fact shows itself markedly as a drastic decrease in internal pressure (and in the cohesion energy) in the nar-row temperature range of glass transition. The experimentally observed drop of internal pressure on the glass transition of PMMA, PS, and poly(vi-nyl acetate) corresponds to an increase in the en-ergy of the chain elastic tension up to 40 cal cm^{-3}.[27] In addition, data obtained by the neutron scattering method show that the sizes of macro-molecular coils in polymer glasses always in-crease 20% greater than those in a nonsolvent.[28] This fact also points to the chain stretch by the p-carcass.

The previously described drop of internal pres-sure[27] and the "free volume," stored in a glass polymer, can be reduced under high pressure ap-plied to the polymer melt.[28] However, this does not result in translation of the system to the equi-librium state, because annealing of the samples compacted under pressure recovers both the ini-tial sizes of macromolecular coils and the "free volume"[28] caused by the return of the system to the normal balance on the elastic forces between p- and s-skeleton elements of the matrix.

Thus, the experimental material available in the literature confirms that glassy polymers exist as the more or less compacted xerogels, whose compatibility with liquids is affected from the structural resistances of the formed p-carcass and s-zones.

CONCLUSIONS

This article presents some important peculiarities of the polymer–liquid blending, emphasizes non-equivalence of the definitions "plasticizer" and "solvent" that are still often used as synonyms, and accounts for the frequent nonadequacy of the solubility parameters for polymers[2] that may be associated with the specificity of a particular blending procedure. There are indirect ways for blending, such as the use of a common solvent or the application of mechanical excitation (e.g.,

rolling or pressing). Experimental results have been attributed to the characteristics of the carcass-sponge structure of "amorphous" polymers. An important property of the carcass-sponge structure is preservation of the polymer matrix in the state with an excess or deficit in entropy. The consideration presented provides the possibility for understanding the phenomena that could not be explained on the basis of statistical physics of structureless polymers.[29]

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