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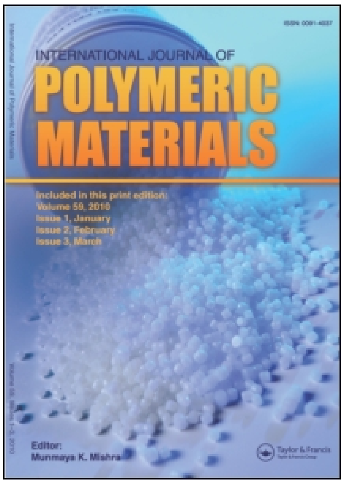

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On Structural Effects and Entropic Factor of Blending Noncrystalline. Polymers with Liquids

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The absence of spontaneous blending of an amorphous polymer with a liquid when their solubility parameters coincide is explained by specific features of the polymer supermolecular skeleton. Such a process requires dissolving the structural skeleton and the availability of the sufficient entropic-donor activity of the liquid. Lack of the above activity rules out the spontaneous process. However, the possibility that the process will take place via an indirect pathways remains because of the specific nature of supermolecular organization of polymer chains.

KEY WORDS Polymer-liquid blending, thermodynamics solubility parameter, supermolecular structure, amorphous polymers.

RESULTS AND DISCUSSION

The coincidence of the solubility parameters (δ) for various liquids is known to ensure their compatibility. The process occurs because of an increase in entropy.[1,2] However, an analogous agreement between the δ values for an amorphous polymer and a liquid does not result necessarily in spontaneous blending. This phenomenon is usually explained by specific interactions following a liquid-liquid, polymer-liquid, or polymer-polymer pattern. The polymer is assumed to be as a high-viscosity liquid.

Up to the present, it was believed that only transient structural elements, with limited life time are formed in noncrystalline polymers.[3] However, the increasing amount of experimental data points to the formation of the permanent supermolecular structure in "amorphous" polymers. As is shown in this work, these structure elements are responsible for some peculiarities of the compatibility of amorphous polymers which in some cases excludes the spontaneous blending. Nevertheless, even in the absence of a spontaneous pathway, a homogeneous blend of a polymer and a liquid can be obtained, if the work is consumed in the destruction of the structural matrix.

Cellulose triacetate (CTA, the acetate number is 62.5%, $M_v = 330\,000$), polymethyl methacrylate (PMMA, $M_n = 140\,000$), and polycarbonate (PC, "Makrolon," $M_v = 25\,500$), which have approximately equal values of the δ parameter (19.0, 19.0, and

19.5 $(J/cm^3)^{0.5}$, respectively), were used in the experiments. According to the general idea,[1,2] the above polymers should be spontaneously compatible with the known plasticizer, dibutyl phthalate (DBP, b.point = 340°C, δ = 19.3 $(J/cm^3)^{0.54}$) because of the entropic factor. However, the glassy films prepared from solutions of these polymers in methylene chloride (MC) show no dissolving when in contact with liquid DBP. Only wetting such films by MC (δ = 19.8 $(J/cm^3)^{0.55}$) makes them sticky, whereas the stickiness is not observed on keeping the polymers in liquid DBP for some months. On the contrary, thin PMMA and PC films break into isolated pieces in DBP in 24 hours, and their quasi-brittle failure takes place in minutes at elevated temperatures (60°C for PMMA and 95°C for PC).

To accelerate blending, granules of commercial PMMA of 2 mm size containing 3–4% of MMA were heated at 100°C (the deglassifying region) in liquid DBP for several hours. The granules were not sticky after their cooling down to room temperature. Heating of the DBP-containing PMMA films with T_g = 30°C[4] in DBP at 60°C (to accelerate relaxation processes, 30 wt.% of plasticizer, DBP, was introduced into these films via DBA solution in MC), results in their fast failure into small pieces. These pieces remain glassy at room temperature for months until a complete evaporation of the DBP liquid layer.

Although the above polymers do not dissolve spontaneously in DBP, they are readily compatible with the plasticizer through a common solution in a proper volatile solvent. Thus according to DSC data, the blends of PMMA with DBP prepared from a toluene solution are completely compatible over a wide range of the component ratios (up to 1:1).[4] We prepared the DBP-containing polymer films through their solutions in MC, evaporating the latter in a dish covered with a flat glass. The DBP content in PMMA and PC samples was 30%, and that in CTA attained 86%. All the films were optically transmittant, did not exhibit the stickiness of the polymer-MC blends and did not dissolve in liquid DBP for many days.

The Figure 1 shows the curves for the relative mass change m/m_0 of the CTA samples containing various DBP amounts in the course of their heating in liquid DBP at 98°C. Note that before weighing, the films were purified from the residual DBP layer by filter paper. As is seen, the change in the m/m_0 parameter is practically completed within 30 hours. An insignificant increase of this value (by 3–4%) for the samples containing 0 and 19% of DBP (curves 1 and 2, respectively) appears to result from the fact that the portion of liquid DBP penetrates into internal microcapillaries and cracks of the films. The samples containing 43, 65, and 85% of DBP lose up to 5% (curves 3 and 4) and 19% (curve 5), respectively, of their initial mass owing to the removal of plasticizer from the films. After the heating of the above samples the DBP content in the respective films is reduced to 40, 61, and 70% and their optical transmittance remains changed. As evidenced by weighing the films after complete extraction of the residual DBP by heptane at 98°C (for heptane δ = 15.36 $(J/cm^3)^{0.55}$), the initial mass of the polymer remains constant as well.

The above results are of great importance, because these cannot be interpreted assuming that the system has not yet reached the equilibrium state due to the retarded relaxation. In addition, the dissolving and swelling of the polymers does not take place either at room temperature or at elevated temperature when the molecular mobility is enhanced. According to the curves in Figure 1, the structural-mechanical

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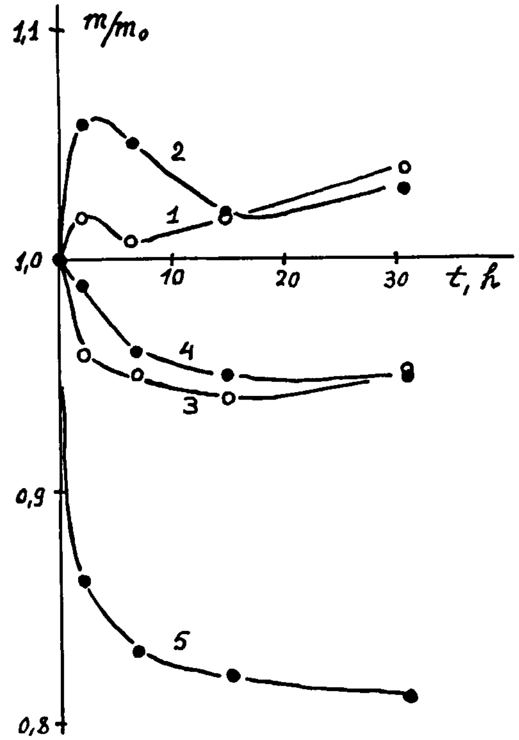

FIGURE 1 The relative mass response for Cellulose Triacetate patterns when heated in Dibutyl Phthalate medium at a temperature of 98°C. The concentration of Dibutyl Phthalate in polymer: 0 (1), 19 (2), 43 (3), 65 (4) and 86 mass % (5).

equilibrium of the film-liquid system is completely established within 30 hours. The absence of dissolving and swelling of the polymers is indicated by the equilibrium amount of DBP.

The above results appear paradoxical. In fact, the polymers and the liquid having the identical δ parameters are completely compatible via a common solvent, suggesting that the DBP chemical potential in the polymers decreases and the driving force for the spontaneous blending of both components exists when these are in immediate contact. Nevertheless in reality, films do not dissolve or swell in large excess of liquid DBP over a wide range of temperatures at either low or high DBP contents in the polymer samples. It is significant that the films, which correspond in their composition and mechanical properties to the gel-like state (more than 50% of DBP),[2,6] are compatible with an additional DBP amount only through the process of their dissolution in MC.

The absence of swelling of CTA films in liquid DBP was confirmed by the diffusion of naphthalene, which was introduced into the films from MC solutions. The naphthalene diffusion rate and diffusivity were determined (using the values of the naphthalene optical density at a maximum of the absorption band at $\nu = 36\ 400$ cm^{-1}) from the plots of the well-known relationship $(1 - D/D_0) = (4/L)(D_i t/\pi)^{0.5}$ in the range $(D/D_0) < 0.5$. Here, D_0 and D are the initial and current values of the optical density, respectively, D_i, L, and t stand for the diffusivity, film thickness, and time, respectively. Heating the films containing 1.4% of naphthalene in liquid DBP at 99°C did not result in a marked naphthalene loss within 10 hours (this loss attained 23% in air with $D_i = 6.8 \times 10^{-13}$ cm^2/s). At the initial naphthalene concentration of 5%, its diffusivity in air is linear with the DBP concentration, which is introduced in combination with naphthalene: $D_i = (1.7\times 10^{-12} + 1.4 \times 10^{-11} C_{\mathrm{DBP}})$ cm^2/s. Consequently, the presence of the plasticizer in the films accelerates considerably the diffusion. Heating the films containing 5% of naphthalene and 5% of DBP showed about equal values of the diffusivity in air and in liquid DBP [(0.75 − 1.00) $\times$ 10^{-11} cm^2/s], suggesting that an increase in the diffusion rate does not correlate with the DBP penetration into the film from the liquid phase.

The absence of spontaneous blending of liquid DBP with polymers (CTA, PC, and PMMA), whose solubility parameters are equal to that of DBP, suggests a similar nature of the supermolecular organization in these polymers. This organization should resist independently from the flexibility and brittleness of the chain package, the equalization of the DBP chemical potential through the dissolution or swelling of polymers. 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 the densest cross-linked molecular network, differing substantially in such behavior from the gels of the 1 type.[2,6]

Gels of the 1 type are known to be formed when polymer chains are sparsely cross-linked either by chemical bonds or by insoluble crystalline bundles. These gels are characterized by the marked reversibility of swelling. The absence of this phenomenon in the systems considered indicates in addition to the presence only the bundles (paracrystalline domains[7]) insoluble in DBP also the existence of a continuous skeleton of these domains bonded to each other. During the formation, the skeleton network should accumulate large amounts of DBP. Once the skeleton is formed, it should exclude the possibility for dissolving and swelling the samples. To the above considerations there corresponds an organization such that only a small fraction of the polymer chain links forms segments of paracrystalline domains, which form thin spherical-shape shells. These sections are grain-shaped and have the structure of a felt (sponge), which is able to absorb solvents and impurities.[7] The overall change in the Gibbs' energy on dissolving such a skeleton material should consist of two parts:

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

where the p and s indexes refer, respectively, to the continuous p-skeleton and to the grains of the sponge s-skeleton.

According to the Equation (1), the different properties of MC and DBP may be explained by a more significant contribution of the entropic terms, $(T\Sigma\Delta S_i^m) > (\Delta H_p^m + \Delta H_s^m)$ for MC, causing the dispersion of the skeleton into a molecular solution. The entropic factor for the DBP-containing systems, on the other hand, prevents dissolving and swelling of the polymers.

In the absence of the spontaneous process, an indirect way exists for blending of DBP with polymers via a common volatile solvent which acts as a donor of entropy. On evaporation in the course of producing the films, the solvent transmits the created

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entropic sites to the plasticizer or to another component that plays the role of the entropic acceptor. Such a transmission is associated with the formation of rigid elements (p-domains), which are stable, mobile and capable of cooperating in the form of the open-work p-skeleton. Various publications claim the existence of rigid structural elements in polymer melts and solutions by the NMR and ESR methods. In particular, the ESR study showed that the above elements appear in solutions of labeled PMMA and PS (nitroxide was attached to the polymer backbone) even at considerable degrees of dilution (the solvent content was 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]

In other words, polymer chains in every cell of the continuous p-skeleton should be considered as a swollen high entropy sponge. The latter is responsible for the accumulation of DBP molecules (as well as those of other impurities), in the places being freed of the solvent molecules in the sponge zones. As a result of this process, the sponge zones remain swollen but contain another filler.

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

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

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

where the g index refers to the carcass of a gel, and the upper p and L indexes characterize the terms, connected with the plastifiizer (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 non-solvent should condense, forming ordered domain and chain zones. Consequently, the p-domains are tightened more closely to form shells that are less permeable 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 on keeping the films for a year even at the DBP initial content as high as 86%.

The matrix that is condensed and ordered due to a solvent change precludes the swelling of CTA films in liquid DBP even at elevated temperature (98°C). The degree of equilibrium swelling attained by macromolecular spatial networks in a liquid, which is a non-solvent for a non-cross-linked macromolecules, increases as temperature rises.[6] However, with the gel-like films a marked loss in the plasticizer is observed (Figure 1, curves 3–5). This appears to be connected with the difference in the coefficients of heat expansion for sponge zones and those of continuous skeleton of strongly bonded *p*-domains. The latter restricts the swollen sponge expansion and creates the conditions favoring the partial removal of DBP.

Clearly, the above way of blending is realized not only with DBP, but for other non-solvents including the crystalline ones. The restrictions arise only when the enthalpic factor of the replacement in the sponge system is opposed by a great change in enthalpy, ΔH_{pb}.

A non-solvent which is compatible with a polymer in an indirect way can be replaced by another non-solvent without qualitative by changing the supermolecular structure of the sample. This is demonstrated by the following experiment. The CTA samples were heated in liquid heptane and water at 95°C, the DBP amount was detected by its optical density of the (36 600 cm^{-1}) absorption band. The DBP diffusivity was determined in a manner like that described for naphthalene. Heating the films containing 1.4% of DBP in air for 50 hours resulted in no significant loss of plasticizer. At the DBP content of 19.0%, its desorption in air is more marked with the diffusivity being equal to 7.5×10^{-13} cm^2/s. About the same D_i value is obtained for DBP diffusion in heptane from the films containing 1.4% of the plasticizer, its loss being relatively low for 50 hours. 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. When the DBP content exceeds 50.0%, the films become completely DBP-free within 1.5 hours.

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

As is seen, therefore, the displacement of both liquids accelerate considerably the removing of plasticizer, although these liquids are poorly sorbed by the polymer and differ in their polarity and in the δ parameters. The action of the liquids occurs by the different structural-dynamic mechanisms, as evidenced by the differences in the diffusivity values and in their effects on the polymer films. Thus, the DBP removal (at its initial content of 55%) by heptane is completed within 1.5 hours and results in no change in the film thickness (35 μm), whereas under the water action, the thickness decreases by a factor exceeding 2, and the process lasts for 30 hours. Obviously in both processes, the skeleton matrix of the polymer experiences mechanical forces that are different in magnitude and directionality.

Both these liquids produce an osmotic swelling pressure in chain-sponge cells of the *p*-skeleton. At a sufficient degree of plasticization, heptane, which is well compatible with the sponge impregnated by the plasticizer, produces the pressure that is capable of sustaining a level of the segmental mobility and the degree of stretch of insulating shells that allows DBP molecules to escape from the carcass cells. Upon the process completion, the dry CTA films hold their initial thickness. This result indicates the presence of voids in the films and a structural resemblance of the sponge

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cells to microporous adsorbents. The impulse NMR study showed independently that the structure typical for microporous adsorbents is present in the plasticized polymers.[9]

As distinct from heptane, water converts DBP-containing CTA gels to ordinary dense films. This process is most likely caused by the fluctuation formation and destruction of water clusters in a hydrophobic chain-sponge medium.[10] The action of cluster hydrophobic forces on surrounding polymer chains results in the arrangement of chain links into mobile hydrophobic slits.[11] Such slits are formed and destructed in chain-sponge zones decreasing the entropic store of the system. Thus, in the course of their fluctuations, the slits perform work on the plasticizer displacement and on the matrix condensation.

Note an interesting example when a non-solvent is substituted by another one in PC films.[12] The films were prepared from MC solutions containing various amounts of the aromatic compound, stilbene (m.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. As this takes place, the entropy store, which was created by the solvent and preserved by stilbene in the PC matrix, is responsible for the enhanced amount of absorbed benzophenone compared to that in the films of pure PC.

Some other ways of blending polymers with non-solvents are known. Thus, styrene polymerization in the presence of pentane, heptane, and octane allows one to produce glassy PS, occluding a great amount of these hydrocarbons.[13,14] The same glasses are prepared, if a PC melt is glassified under pressure of cyclohexane vapors.[13-15]

The procedure of MMA polymerization in the presence of a great quantity of plasticizers was proposed for producing light-protective self-clarifying PMMA glasses (containing additives of photochrome compounds), which exhibit a fast restoring of optical transmittance. With the use of plasticizers, 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 is revealed by the accumulation of plasticizer inside the chain-sponge zones of the matrix, which are encapsulated in cells of the rigid *p*-skeleton.

The role of the entropic factor in the formation of these superstructures is clearly indicated in chemical cross-linking of macromolecules in solutions. For example, PS-based microporous adsorbents, exhibiting a high degree of swelling in non-solvents, can be prepared by adjusting the rate of chain cross-linking relative to that of the relaxation of the supermolecular skeleton.[17]

It is significant that polymer chains tie the zones of *p*- and *s*-skeletons (so that links of a certain chain fit into both of these skeletons) rather than form a mechanical mixture of dissimilarly structured particles. Ordering a portion of links in *p*-skeleton domains creates structures providing mechanical obstacles for ordering other links of the same chains inside of the sponge *s*-zones.

In accordance with the above considerations, the thermodynamic equilibrium for an endless skeleton body formed from a solution $\Delta G_g = \Delta G_p + \Delta G_s = 0$ should have the form such that the negative term $\Delta G_p = \Delta H_p - T\Delta S_p$ (which is responsible

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for the stability of a whole supermolecular continuous spatial lattice) is opposed by the positive term $\Delta G_s = \Delta H_s - T\Delta S_s$ (which is responsible for the attainment of the equilibrium state in the spontaneous structurization of a polymer solution, yielding a gel). Hence, it follows that the factor

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

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

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

Thus, the system makes its structure compatible with a non-solvent as a result of storing the elastic energy and decreasing the compatibility with a solvent. The structural memory obtained by the system under this conditions may be realized (for rather sparsely cross-linked polymers) as considerable swelling even in such non-solvents as water and alcohols.[17]

The same change in entropy should accompany the formation of the so-called aerogels on sublimation of a solvent from frozen polymer solutions, studied in Reference 18. In accordance with expression (2), we have for this case

$$-\Delta S_s = \Delta S_p + (-\Delta H_p - \Delta H_s)/T.$$

The ΔH_p and ΔS_p terms should be virtually independent of temperature, because they are the characteristics of the openwork of quasi-crystalline skeleton. In the absence of specific interactions between macromolecules and a solvent, the ΔH_s term should be insignificant and negative because of the thickening sponge material relative to a liquid. Consequently, freezing a solution and decreasing a temperature of skeleton assembly increases a negative change in entropy of a polymer-chain sponge.

A microporous gel possessing the developed inner surface of 1000 m^2 (which equals that of a cross-linked PS gel) was prepared from a PS solution in benzene.[18] Thus, both on cross-linking a polymer and on sublimation of a solvent, a forced decrease in entropy of the chain-sponge system takes place and, a solvent is converted into a non-solvent.

Because of the delated matrix and reduced entropy, dry aerogels are thermodynamically unstable and are thickened to form usual polymer glasses when heated.[19] Thickening also occurs when a solvent is evaporated from a non-frozen gel and as mentioned above under the water action on DBP-containing CTA gels. Note that spontaneous thickening of a skeleton gel does not result in complete collapse of polymer chains inside *s*-zones, because the *p*-skeleton resists this process. As a result of force balancing both skeleton structures, property variations of the polymer glasses

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appear. Indeed, the specific features of particular physical interactions and the rate ratios of the relaxation processes at the thickening stage is 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 cross-linked chains, "polysorbs," compose larger size (70 nm) globules.[25]) Moreover, the electron microscopic 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 mentioned above, the skeleton structure fixed by *p*-domains prevents the chains from the complete collapse in a glassy polymer. This fact shows itself as a drastic decrease in internal pressure (and in the cohesion energy) in the narrow temperature range of glass transition. The experimentally observed drop of the internal pressure on glass transition of PMMA, PS, and polyvinyl acetate, corresponds to an increase in the energy of the elastic chain tension of up to 40 cal/cm^3.[27] In addition, the data obtained by the neutron scattering method show that the sizes of macromolecular coils in polymer glasses are always by 20% larger than those in a Θ-solvent.[28] This indicates a considerable strain of chains fixed by the *p*-skeleton.

The above drop of internal pressure[27] and the empty space stored in a glass[28] can be reduced under the action of external pressure on the plymer melt. However, this effect is not due to approaching to the equilibrium state, because on a following aneal line of the samples thickened under pressure, restores both the initial sizes of macromolecular coils and the "free volume" store.[28] This reflects the return to the state of undistorted distribution of the elastic forces between *p*- and *s*-skeleton elements of the matrix.

Thus, the experimental evidences available in the literature confirm the concept that glassy polymers are more or less dense gels with all ensuing consequences regarding their compatibility with liquids.

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CONCLUSIONS

The unusual characteristics of polymer-liquid blending were presented. The conclusion has been reached that the terms "plasticizer" and "solvent" are not equivalent. It was shown that the literature values of the solubility parameter for polymers cannot explain the polymer-liquid phenomena, because compatibility depends on the specifics of the blending method. The compatibility sometimes cannot be achieved spontaneously. There are, however, indirect ways that may result in compatibility, such as the use of common solvent or application of mechanical forces (e.g. rolling or pressing), etc. The experimental results have been attributed to the characteristics of the carcass-sponge structure of "amorphous" polymers. The nature and control of this superstructure warrants comprehensive evaluations because depending on its character, it can stabilize the matrix with large excesses or deficits of entropy. This, in, turn provides the possibility for advanced theoretical analysis and development of processes which could not be foreseen on the basis of statistical physics of structureless polymers.

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