The Influence of Thickness of Polymeric Stationary Phase on Its Properties Determined by Gas Chromatography

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ABSTRACT: By the use of gas chromatography for some amorphous and crystalline polymers the influence of the thickness of a polymer film as a stationary phase and of the nature of the support on glass transition temperatures and degrees of crystallinity was investigated. It was shown that the value of retention volume depends on film thickness. In some cases there is also dependence on film thickness of glass temperature, which increases with diminishing thickness. The degree of crystallinity decreases when film thickness decreases independent of the nature of the support (glass or Teflon). The effects discovered are explained on the basis of the assumption that the surface polymer layer consists of two parts: (1) a true adsorption layer, where all macromolecules are directly connected with the surface; and (2) a loosely packed layer connected to the first by cohesion forces. For films of different thickness the excess thermodynamic functions of mixing were determined and it was shown that they are dependent on film thickness.

In some fundamental work it was shown that when polymer is used as the stationary phase it becomes possible to find out its glass transition point or melting point and degree of crystallinity and to calculate the thermodynamic interaction parameter and excess entropy of mixing.[1-7] However, it is worth noting that parameters found by gas chromatography have to do with comparatively thin polymer films on solid surfaces, and therefore it is reasonable to assume that the interface can influence the properties of such films. Really, in some of our works[8,9] we have established the strong influence of the interface on such important properties of thin polymer layers as transition points, heat capacities, packing density, and others.

Our main task here is to apply the gas chromatography method to study the influence of stationary polymer phase thickness on glass transition points, degree of crystallinity, and thermodynamic interaction parameter polymer–solvent.

Method

Experimental chromatograms were obtained by use of chromatograph model "Chrom 4" (Czechoslovakia) with ionization-flame detector. Nitrogen was used as a carrier gas. The measurement of carrier gas rate was performed by a soap buble flowmeter, $V_r = V_0T_{col}/T_{flow}$, where V_0 is the rate measured at the temperature of the column T_{col} and T_{flow} is the flowmeter temperature. The pressure in the column in all cases does not exceed 5–10 mm. The pressure difference at the inlet and the outlet was 0.1 mm and the correction for carrier gas compressibility was omitted.

Polymer phase was brought from solutions in methylene chloride in the course of slow evaporation of solvent at continuous stirring of solution with immerse glass beads. The average film thickness was calculated from values of solid surface area and polymer volume. The surface area for glass beads was estimated by comparison of reduced component retention times by sample under investigation and standard sample at the same conditions (pressure difference, temperature, volume rate of carrier gas) according to equation

$$t_{R_1}'/t_{R_2}' = S_2/S_1$$

where t_{R_1}' and t_{R_2}' are the reduced retention times for sorbate for sample and standard and S_1 and S_2 are the corresponding surface areas. The glass beads of diameter 30–40 μ were chosen, their surface being determined by calculation. As a Teflon support, Teflon crumbs of diameter 0.5 mm and height 1 mm were taken, surface area being calculated as the cylinder area.

The chromatographic columns were filled as a solid support with glass beads (0.3–0.5 mm) or Teflon crumbs with thin surface polymer layers obtained by casting from solutions. Samples taken were polystyrene (PS), M_{av} = 190000, poly(methyl methacrylate) (PMMA), M_{av} = 700000, poly(ethylene glycol adipinate) (PEGA), M = 2000, and poly(ethylene glycol) (PEG), M = 6000 and 15000. Some PS films were obtained during adsorption from solutions of different concentration in toluene. For this case the film thickness corresponds to its equilibrium value. In our study we have used mainly glass beads as nonporous support. For porous supports the film thickness calculated may vary by a factor of more than 500[10] due to polymer penetration into pores.

We have extrapolated the dependence of retention time on peak height to its zero value. The initial peak height corresponded to the probe size 0.05 μl. The volume rate of carrier gas flow was in the region 2–10 ml/min. For all polymers (except PEGA) the retention values in this rate range were constant. For PEGA there occurred a slight dependence of retention time on flow rate, the extrapolation to zero rate being made for this case.

Results and Discussion

1. Glass Temperatures. The dependence log $V_g - 1/T$ for PS films and different sorbates is shown in Figure 1. It is seen that the glass temperature of PS, which corresponds to the first inflection on the curve[3] in a given range of thicknesses (3430–200 nm), does not depend on film thickness for either glass or Teflon surfaces. Meanwhile for PS on a glass surface the transition point is higher (89°) in comparison with a Teflon surface (82°). For PMMA these temperatures are correspondingly 112 and 104°. Thus it is seen that the surface nature influences the glass temperatures.

The lack of glass temperature dependence on film thickness, at least in the thickness interval studied, seems to be at variance with many literature data where it was shown that glass temperature does depend on film thickness (see, e.g. ref 8). The increase in the glass temperature for filled polymers is usually connected with restrictions of molecular motion in adsorption layers on a solid surface.[8,9] These effects were discovered by measurements of change in molecular mobility (calorimetry, dielectric, NMR, and me-

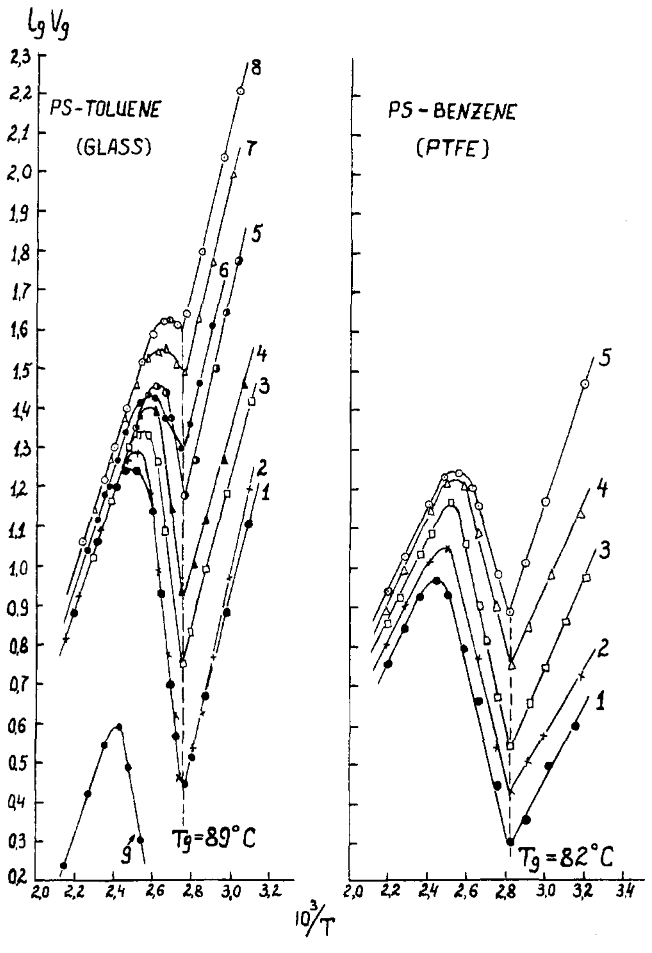

Figure 1. Dependence of V_g on $1/T$ for PS films of different thickness on glass and Teflon surfaces. Film thickness on glass: (1) 3430 nm, (2) 2900 nm, (3) 2240 nm, (4) 1270 nm, (5) 570 nm, (6) 400 nm, (7) 283 nm, (8) 200 nm, (9) 1000 nm (sorbate,heptane). Films thickness on Teflon: (1) 2900 nm, (2) 2100 nm, (3) 1500 nm, (4) 850 nm, (5) 570 nm.

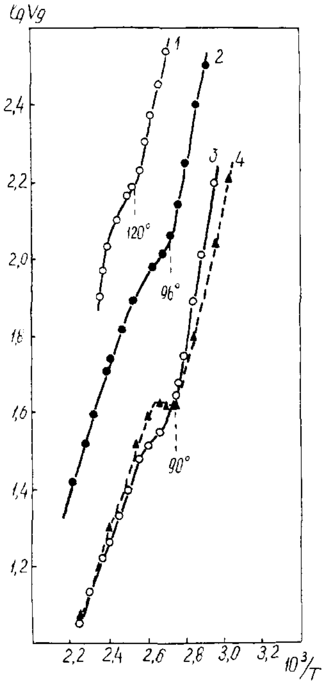

Figure 2. Dependence of log V_g on $1/T$ for films obtained by adsorption from toluene solution (1–3) and obtained by solvent evaporation (4). Film thickness: (1) 23 nm, (2) 80 nm, (3) 280 nm, (4) 283 nm. Sorbate, toluene.

chanical relaxation). In gas chromatography the glass temperature determination is based on changes in small molecule sorption in polymer films at the glass temperature and is connected with the increase of sorbate molecule diffusion in polymer film from the very outset of molecular motion. For the thicknesses under consideration the films can be considered to consist of two layers. In the first adsorption layer macromolecules are directly connected with the surface; the molecules in the second layer do not have direct adhesion bonds. Since at the glass temperature the diffusion can proceed only in upper film layers, its structure determines the curve inflection log $V_g - 1/T$. It is probable that, for films of thickness comparable with the adsorption layer thickness, change in the glass temperature will take place. Really, such films were obtained in the case of adsorption of PS from solution in toluene at different concentrations. In this case the film thickness corresponds to equilibrium adsorption at different points of the adsorption isotherm.

Figure 2 shows the dependence log $V_g - 1/T$ for some adsorption films. It is seen that the glass temperature increases with decrease in adsorption film thickness and is 30° higher than for thick films obtained by solvent evaporation. When equilibrium concentration of solution during adsorption increases, the film thickness increases and glass temperature decreases. These phenomena can be explained on the basis of ideas developed by us earlier.[11,12] At small concentration of solution in the adsorption process only isolated macromolecular coils participate and the number of their contacts with the surface is high enough. At higher concentration the interaction between dissolved macromolecules begins to play an essential role, and, as a result, some molecular aggregates are formed. As was proved directly by experiment, these aggregates also can be adsorbed by the surface.[13] In this case both the number of contacts of adsorbed macromolecules with the surface and the density of the adsorption layer are diminished. This leads to a stepwise decrease in glass transition temperature.

Therefore in using gas chromatography for polymer investigation one must have in mind that the properties of surface films are dependent on the method of their preparation.

The Degree of Crystallinity. Figure 3 shows the curves log $V_g - 1/T$ for crystallizing oligomers PEGA and PEG. These curves are typical for crystalline polymers above the glass temperature.[6] Using the data given in Figure 3, the degree of crystallinity was calculated according to

$$\text{degree of crystallinity, \%} = \left[1 - \frac{V_g(\mathrm{B})}{V_g(\mathrm{E})}\right] \times 100$$

where $V_g(\mathrm{B})$ is specific retention volume at point B and $V_g(\mathrm{E})$ is the same at point E for amorphous polymer. Figure 4 shows the dependence of calculated degrees of crystallinity on film thickness. It is seen that the crystallinity decreases with decrease in film thickness for both systems independent of the nature of the surface. The degree of crystallinity for films heated first to a temperature above the melting point is higher than for films cast from solution in methylene chloride and dried under vacuum below the melting point. For PEG there arises an additional transition at 35° which is absent for melt-crystallized polymer. The origin of this transition is not clear and we suppose it to be connected with the melting of disordered molecular aggregates, which are present in PEG solutions[14] and deposited on the surface.

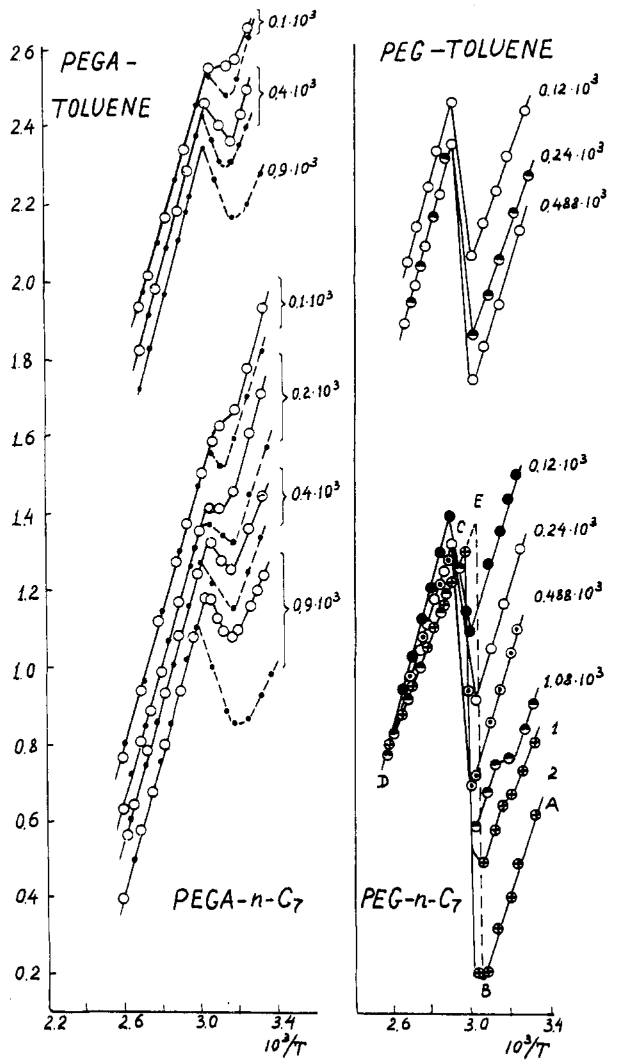

Figure 3. Dependence of log V_g on $1/T$ for PEGA and PEG films on glass. Figures near the curves indicate film thickness, in nm. For PEG: (1-PEG) 6000 film, dried under vacuum below melting point; (2-PEG) 15000 film, heated above mp sorbate, heptane.

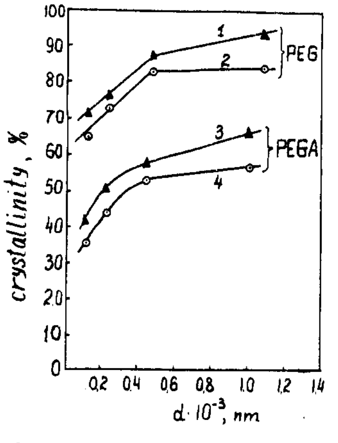

Figure 4. Dependence of degree of crystallinity on film thickness for PEG (1, 2) and PEGA (3, 4). Curves 1 and 3 are for heated films.

In principle, the observed retention volume for polymer stationary phases may be considered as a sum of three partial retention volumes connected with dissolution of sorbate in the polymer phase and its adsorption on the polymer surface and on the free support surface:

$$V_r = k_b m + k_s A_s + k_s' A_s' \qquad (1)$$

where k_b, k_s, and k_s' are distribution coefficients for dissolution of sorbate by amorphous phase, adsorption by polymer surface, and free surface, and A_s and A_s' are polymer and free support surface areas. If we neglect the contribution of $k_s'A_s'$, the equation for the calculation of crystallinity degree may be written as

$$\text{degree of crystallinity, \%} = \left[1 - \frac{(V_g(\mathrm{B}) - k_s A_s/m)}{(V_g(\mathrm{E}) - k_s A_s/m)}\right] \qquad (2)$$

Where $V_g(\mathrm{B}) = k_b(x/m) + (k_s A_s/m)$ and $V_g(\mathrm{E}) = k_b + (k_s A_s/m)$. m is the weight of stationary phase and x is the weight of the amorphous phase in point B.

The value $k_s A_s$ is usually determined by extrapolation of dependence V_g on $1/V_L$ (V_L is the volume of the stationary phase) to $1/V_L \rightarrow 0$.

If we suppose that the increase of V_g with the decrease of film thickness for PEGA is determined by the contribution of adsorption onto polymer surface, we can make such an extrapolation for the systems PEGA–heptan and PEGA–toluene to evaluate the values of $k_s A_s/m$ for different film thicknesses. However, the calculation of the crystallinity degree according to eq 2 for such a case leads to the unreal high values (nearly 90%) which do not correspond to the data of scanning differential calorimetry (60%). Besides, the crystallinity degrees calculated according to eq 2 for the systems PEGA–heptane and PEGA–toluene differ by 20% whereas the same calculation according to eq 1 gives the difference no more than 5%. These calculations allow the supposition to be drawn that the increase of V_g with the decrease of film thickness is determined not by contribution of adsorption onto polymer surface but by the influence of the surface on the polymer structure and its dependence on film thickness.

The decrease in the degree of crystallinity with the decrease in film thickness we explain by the formation of an adsorption polymer layer at the interface with solid. In accordance with our earlier work[9,10] in such a layer the macromolecules have diminished molecular mobility and possess smaller density of packing due to conformational restriction near the interface. The restriction imposed on the conformation of surface polymer molecules leads to the changing of crystallization conditions, and the degree of crystallinity will be smaller when the layer thickness is smaller (see, e.g., ref 15).

The Thermodynamic Interaction of Polymer–Solvent. The adsorption layer at the interface with solid has to affect the thermodynamic values such as excess molar free energy, enthalpy, and entropy of mixing. For the calculation of these parameters we can use the general expressions of gas–liquid chromatography which connect the activity coefficients of sorbate at infinite dilution and retention volume for equilibrium absorption:[7]

$$\ln\left(\frac{a_1}{w_1}\right)^{\infty} = \ln\frac{273R}{V_g P_1 M_1} - \frac{P_1}{RT}(B_{11} - V_1)$$

where P_1 and V_1 are the saturated vapor pressure and the molar volume of sorbate at the column temperature, B_{11} is the second virial coefficient, V_g is the absolute specific retention volume, and M_1 is the molecular weight of sorbate. The interaction parameter can be expressed as

$$\chi = \ln\frac{273Rv_2}{P_1 V_1 V_g} - \left(1 - \frac{V_1}{M_2 v_2}\right) - \frac{P_1}{RT}(B_{11} - V_1)$$

Here M_2 is the molecular weight of polymer and v_2 is the specific volume of polymer.

Table I
Activity Coefficients (Weight Fraction) $(a_1/w_1)^\infty$ and Parameter χ of Sorbates at Infinite Dilution in PS and PMMA

Polymer–solvent	Film thickness, nm	$(a_1/w_1)^\infty$ 150°C	175°C	200°C	χ 150°C	175°C	200°C
PS–toluene	200	6.02	5.76	5.85	0.40	0.357	0.345
	283	5.80	5.64	5.64	0.393	0.35	0.33
	400	6.27	6.20	6.20	0.47	0.44	0.42
	570–3430	6.90	6.88	6.92	0.615	0.58	0.56
		6.28[a]	6.27[a]	5.53[a]	0.52[a]	0.49[a]	0.336[a]
		5.22[b]	5.29[b]	5.34[b]	0.334[b]	0.319[b]	0.301[b]
		4.40[c]	4.30[c]	4.10[c]			
PS–benzene	570–3430	6.45	6.44	6.30	0.552	0.51	0.36
		5.76[a]	5.31[a]	5.81[a]	0.435[a]	0.313[a]	0.304[a]
		5.44[b]	5.67[b]	5.81[b]	0.378[b]	0.382[b]	0.278[b]
		4.29[c]	4.10[c]	3.97[c]			
PS–*n*-heptane	1000	18.5	18.4	19.0	1.327	1.28	1.26
PMMA–xylene			11.1 (203°C)			1.04 (203°C)	

[a] In Teflon. [b] Reference 18. [c] Reference 10.

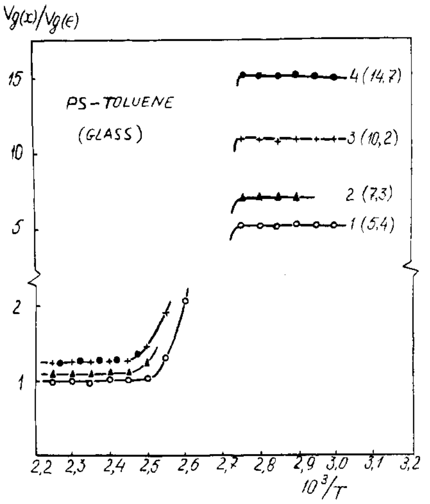

Figure 5. Dependence of $V_g(x)/V_g(e)$ on $1/T$ for films of different thickness: (1) $V_g(5)/V_g(1)$, (2) $V_g(6)/V_g(1)$, (3) $V_g(7)/V_g(1)$, (4) $V_g(8)/V_g(1)$. Figures in the parentheses indicate the ratio $g(x)/g(e)$.

These equations were used in some work where the interaction polymer-solvent was studied.[7,10,16-23] The influence of film thickness on V_g values for PS was studied.[22] In the range 40–250 Å no change in V_g for film on Cromosorb W was found. The reason for this behavior is unclear, as the thicknesses 40–250 Å are less or equal to adsorption layer thickness with changed properties. We connect this with some uncertainty of calculation of film thickness on the porous sorbent.[23]

In our study we have used glass beads, so the film thickness should be found without any difficulty. From Figure 1 it is seen that for PS films on glass the values V_g in the thickness range 570–3430 nm are situated on the one curve after the second inflection point. This shows that in a given thickness range equilibrium absorption really takes place. It is seen also that here the polymer–solvent interaction does not depend on film thickness. However, during transition from large to small thickness there is some increase in V_g. We believe this increase is not connected with solvent adsorption on free surface. From Figure 5 it is seen that the ratio of V_g for very small thicknesses to V_g for other thicknesses does not change with temperature in the equilibrium absorbtion region; i.e., the absorption effects on the free surface are absent[20] and contribution of the third term in eq 1 can be neglected. However, for relatively thick films the essential contribution in V_g may give the second term, connected with sorbate adsorption onto polymer surface. Having supposed that below glass temperature only adsorption onto polymer surface takes place we have calculated its value at temperatures above the second inflection on

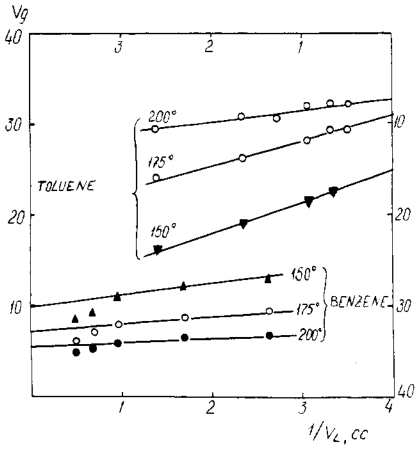

Figure 6. Dependence of V_g on $1/V_L$ for films of PS on Teflon.

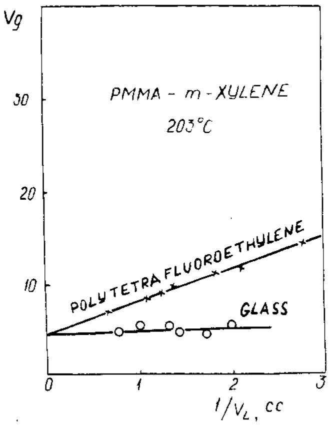

Figure 7. Dependence of V_g on $1/V_L$ for films of PMMA on glass and Teflon.

Table II
Excess Thermodynamical Function of Mixing for Poly(ethylene glycole adipinate) (Mol Wt 2000)

		n-Heptane			Toluene		
Film thickness, nm	T, °C	ΔG_m, kcal/mol	ΔH_m, kcal/mol	ΔS_m, cal/(mol deg)	ΔG_m	ΔH_m	ΔS_m
10×10^2	72	0.796	1.64	2.42	−0.863	−0.596	0.77
	84	0.78			−0.877		
	98	0.74			−0.883		
4.4×10^2	72	0.52	0.645	0.385	−0.996	−0.546	1.31
	84	0.509			−1.015		
	98	0.501			−1.031		
2.2×10^2	72	0.42	−0.446	−2.5	−1.015	−0.317	2.02
	84	0.46			−1.035		
	98	0.48			−1.068		
1.1×10^2	72	0.25	−1.59	−5.3	−1.14	0.06	3.45
	84	0.322			−1.173		
	98	0.378			−1.217		

Table III
Excess Thermodynamical Function of Mixing for Poly(ethylene glycol) (Mol Wt 15000)

Film thickness, nm	T, °C	ΔG_m, kcal/mol	ΔH_m, kcal/mol	ΔS_m, cal/(mol deg)
		n-Heptane		
10.8×10^2	72	0.038	1.84	5.22
	84	−0.024		
	98	−0.097		
4.88×10^2	72	−0.026	1.737	5.0
	84	−0.063		
	98	−0.097		
2.4×10^2	72	−0.067	0.596	1.86
	84	−0.063		
	98	−0.097		
1.2×10^2	72	−0.211	−0.397	−0.54
	84	−0.204		
	98	−0.197		
		Toluene		
4.88×10^2	72	−1.48	−1.042	1.28
	84	−1.501		
	98	−1.515		
2.4×10^2	72	−1.48	−1.042	1.28
	84	−1.501		
	98	−1.515		
1.2×10^2	72	−1.66	−0.993	1.93
	84	−1.69		
	98	−1.708		

curves log $V_g - 1/T$. This was made for films of thickness 200–570 nm by extrapolation of this dependence to higher temperatures. It was found that for a film of 200 nm accounting for the contribution of adsorption lowers the value V_g at 150° only by 5% and at 200° by 2%. At the same time the value V_g for 200 nm film is higher by 15–18% in comparison with 570 nm film. This shows the obvious increase in V_g with the decrease of film thickness. The increase in V_g can be connected with the influence of the surface polymer layer. At small thicknesses the fraction of adsorption layer increases and it can influence the V_g determined, as contribution of solvent adsorption at the polymer–surface interface can be neglected (in a given thickness range). The large value of V_g probably shows that the adsorption layer has a more loose structure and as a consequence the solubility in it is higher. A sharp increase of V_g was found for films (thickness 80 and 23 nm) obtained during adsorption of PS from toluene solution (Figure 2). However, for such a thin film the contribution of adsorption at gas–polymer and polymer–surface interfaces cannot be neglected.

For a Teflon surface an increase in film thickness leads to an increase of V_g (Figure 1). At the same time extrapolation of V_g to infinite film thickness leads practically to the values of V_g at a glass surface (Figure 6). The same dependence of V_g in the region of equilibrium absorption was discovered for PMMA films (Figure 7). We must note that the same increase of V_g was described in ref 18 for squalane on a Teflon surface.

We have calculated also activity coefficients (a_1/w_1) and χ taking into account the contribution of adsorption in V_g for PS films with thickness 200–570 nm (see Table I). For comparison some literature data are given. It is seen that values (a_1/w_1) and χ diminish with a decrease in film thickness at least in the region 200–570 nm. This is in accordance with new data published in ref 24 concerning the influence of polymer film thickness on its thermodynamic properties. It was shown[24] that the retention volumes obtained with capillary columns (film thicknesses 10^4–10^5 Å) for many systems were always lower in comparison with columns (film thickness 10^2–10^3 Å). Such a difference was also connected with different morphology or degree of ordering in thin films adsorbed onto solid surface and in bulk polymer. We must recall here that such differences in properties of surface polymer films and polymers in bulk are carefully investigated in an early work by Lipatov and coworkers.[8] For PEGA and PEG films we have calculated the excess thermodynamic functions of mixing free energy, ΔG_m, enthalpy, ΔH_m, and entropy, ΔS_m, according to the equation given in ref 2 (see Tables II and III). For the calculations we have used the value of the thermodynamic segment molecular weight 3000, as beginning from this molecular weight the value V_g does not depend on molecular weight (Figure 8). From the data given in Tables II and III it is seen that excess free energy of mixing in the system PEGA–toluene and PEG–toluene is negative and diminishes with diminishing film thickness. Such a change ΔG_m shows the increase in solubility of polymer with the decrease of film thickness. This can be connected with the formation of an adsorption layer and its influence on more distant layers. As a result of adsorption interaction with the surface and restriction of molecular mobility, the density of packing near the surface diminishes more when the

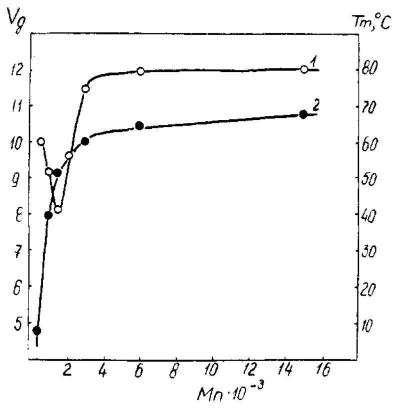

Figure 8. Dependence of V_g (curve 1) and melting point (curve 2) on molecular weight for poly(ethylene glycols). Sorbate, heptane; temperature, 82°C.

film thickness is smaller. This leads to the increase in solubility in good agreement with direct sorption data.[9]

So the data considered above show that the surface nature and the film thickness have an essential influence on the thermodynamic polymer–solvent interaction. There is a need to take these results into account in gas chromatography. From the other side it is evident that this method may become useful for the investigation of these influences on properties of the stationary polymeric phase.

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Mixed-Crystal Infrared Studies of Annealed Poly(ethylene) Single Crystals

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ABSTRACT: The annealing of mixed crystals of poly(ethylene) and poly(ethylene-d_4) results in a transformation, starting at about 100°C, from (110) to (200) folding. This is correlated with the onset of chain motions associated with crystal thickening and is accompanied by spectroscopic evidence for frozen-in chain disorder in the transition region. These results suggest that the fold organization which is stabilized by crystallization from a solvent is not necessarily that which is most stable with respect to the bulk state. In addition, they show conclusively that segregation cannot account for the spectroscopic results on mixed single crystals, as had been proposed; nor can random re-entry be considered a predominant mode of chain organization in single crystals.

Since Keller[1] discovered lamellar single crystals of linear poly(ethylene) grown from dilute solution, and suggested that the long-chain molecules had to fold in order to be accommodated in the crystal, the nature of the chain organization in such crystals has been one of the most controversial problems in the field of polymer science. Flory[2] and Mandelkern[3] have proposed that the re-entry of chains on the surface is predominantly random (the "switchboard" model), while Keller,[4–6] Lindenmeyer,[7] and Kawai et al.[8] have suggested that chain folding occurs with adjacent re-entry in crystallographic planes.

Some years ago a technique was proposed by Tasumi and Krimm[9] to resolve this question, namely mixed-crystal spectroscopy. In this method, poly(ethylene) (PEH) and poly(ethylene-d_4) (PED) are cocrystallized and the pattern of chain organization is deduced from the nature of the band splittings in the infrared spectrum. These splittings arise from interactions between neighboring like chains, and therefore provide a probe of the local environment of the molecules. If, for example, a small amount of PED is cocrystallized with PEH, then chain folding with adjacent re-entry along (110) planes gives rise to PED doublets of about half the splitting as in pure PED, whereas singlets result if the folding is along (200) planes [or (020)] or if random re-entry occurs. The latter two possibilities can be distinguished by analyzing the splittings associated with the PEH molecules, which will be smaller in the case of random re-entry.

These proposals were tested experimentally by Bank and Krimm.[10] By comparing the results on mixed crystals of PEH/PED with those on comparable mixed n-paraffin systems, they could demonstrate conclusively that random re-entry was not a significant component of polymer folding in the crystalline regions. Their results showed that in di-