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Excess viscosity and glass transition

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Abstract

Literature data on the viscosity of solutions of poly(butyl methacrylate) (PBMA) and poly(methyl methacrylate) (PMMA) in diethyl phthalate (DEP) for different temperatures, including the range around and below T_g, the glass transition temperatures of the pure polymers, were evaluated by means of an approach that uses surface fractions as composition variables. The discussion of these results together with information on solutions of the isomeric polymers, poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PM(A)), in the same solvent testifies that the previously published relations remain valid for $T < T_g$. They enable the determination of viscosities of the pure polymers below T_g by extrapolating the solution data to vanishing solvent content. The temperature dependencies of the data obtained in this manner demonstrate that the viscosity of PBMA rises upon cooling as expected according to the WLF equation, whereas the increase is lower by several orders of magnitude for PMMA and PVAc. These observations and the temperature dependencies of the system-specific parameters of the present approach are discussed in detail. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Solution viscosities; Mixing rule; Glass transition

1. Introduction

The prediction of the viscosities of mixtures from the properties of the pure components is of great practical interest and theoretically very challenging. Numerous relations were reported in the literature [1–10], but none of them seems to be general. We have, therefore, investigated possible reasons for the lack of universality. According to physical considerations, this trouble could result from an inappropriate choice of the composition variables, which are normally either weight or volume fractions. In view of the fact that energy dissipation should take place at the interfaces of molecules we have dealt with the problem in terms of surface fractions. The validity of the theoretical approach originating from these considerations was exclusively tested by means of already published experimental material.

The first binary systems to which we have applied the new concept [11] were mixtures of low molecular weight compounds. It turned out that all typical experimental results can be described quantitatively by means of a geometric factor and a term that accounts for specific interactions between the different types of molecules. The former parameter measures the different surface/volume ratios of the components and the latter is closely related to the thermodynamics of mixing.

In the next step we studied the applicability of the approach to mixtures of homologues [12]. For solutions of different high molecular weight poly(dimethylsiloxane)s in the corresponding pentamer, it has become clear that an additional parameter for mixtures that contain macromolecules is required. The reason lies in the flow mechanism of such systems, which changes from non-draining behavior at low polymer concentrations (joint movement of solvent and segments inside the polymer coil) to fully draining at high polymer content. A quantitative description of all experimental data is again possible by means of physically meaningful parameters.

In order to make the approach more general we extended the study to ordinary polymer solutions [13]. The restrictions of homologues (identical interaction between all species) are discarded and special effects resulting from special interactions between the components are taken into account. This modified situation requires an additional parameter for a quantitative description of the experimental findings. Its contribution is, however, rather little — as compared with that of the other terms — and normally represents only a small correction.

With all systems investigated so far the mixtures remain liquid over the entire composition range. In the case of

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polymer solutions and ambient condition this fact excludes most of the polymer solutions of practical interest, since the majority of polymers represent glassy solids at room temperature. For this reason the performance of the present concept under such conditions is studied and one item of particular interest consists in a theoretically justified extrapolation of the viscosities of concentrated polymer solutions (that can still be accurately measured) to the solvent free state of the glassy polymer (where reliable data are hard to obtain).

2. Theoretical background

The zero shear viscosities η of binary mixtures as a function of composition are often discussed in terms of the excess viscosities defined by the mixing law proposed by Arrhenius [2] in terms of volume fractions φ of component 2 as

$$\Delta\ln\eta = \ln\eta - (1-\varphi)\ln\eta_1 - \varphi\ln\eta_2 \tag{1}$$

where η_1 and η_2 are the viscosities of the pure components. The conversion of theoretical consideration concerning the dependence of η on the surface fractions of the solute into the dependence of the excess viscosity on the volume fraction φ of the polymer yielded [13]

$$\Delta\ln\eta = \left\{\delta[\gamma(1+\gamma\varphi)^2 - (1-\varphi)(1+\gamma)] + 2\alpha(1+\gamma)^2\varphi \right.$$
$$\left. + [\eta]\rho(1-\varphi)\left[\frac{(1+\lambda e^{-\lambda[\eta]\rho\varphi})}{1+\lambda}\right]\right\}\frac{\varphi(1-\varphi)}{(1+\gamma\varphi)^3} \tag{2}$$

The viscosities of the pure components enter the above relation via δ, which is defined as

$$\delta = \ln\eta_2 - \ln\eta_1$$

The geometrical parameter γ was introduced to measure the differences in the ratios of the molar surfaces F and the molar volumes V according to

$$\gamma = \frac{F_2/V_2}{F_1/V_1} - 1 \tag{4}$$

For mixtures that contain low molecular weight components or polymers below their entanglement molecular weight, the γ values determined from experimental data agree reasonably well with predictions resulting from tabulated increments of molar volumes and surfaces [14]. Entanglements between the chains of high molecular weight polymers modify the flow behavior and lead to additional friction. For the present description this corresponds to an augmentation of γ over the purely geometrical expectation [13]. The parameter α stands for the hydrodynamic interaction between the components in the limit of vanishing solvent content (fully draining coils) and measures the deviation of η_{12}, the friction between unlike components, from the geometric mean of η_{11} and η_{22}, the friction between like molecules. Similar to γ it depends on the number of entanglements per polymer chain [13].

The intrinsic viscosity $[\eta]$ of the polymer in the solvent of interest specifies the concentration regime within which the change in flow mechanism takes place. Eq. (2) contains this information twice: in terms of the maximum chain overlap $[\eta]\rho$ (obtained by multiplying the intrinsic viscosity with ρ, the density of the pure polymer) and in terms of λ defined as

$$\lambda = \frac{[\eta] - [\eta]_\Theta}{[\eta]_\Theta} \tag{5}$$

where $[\eta]_\Theta$ refers to theta conditions. This additional parameter is of minor importance only, and needs to be considered for thermodynamically very good solvents where the polymer coils change their spatial extension considerably with the composition of the system, from highly expanded on the solvent side to unperturbed close to the pure polymer. For theta systems the expression in the square bracket in the second line of Eq. (2) reduces to unity.

In view of the many extra effects that must be taken into account with polymer containing systems one requires the surprisingly low number of two (γ and α) to three (in some cases also λ) adjustable, physically meaningful parameters for their adequate viscometric description. This statement holds true, if the intrinsic viscosity of the polymer in the solvent of interest is known or can be calculated by means of the Kuhn–Mark–Houwink relation. In case this information is inaccessible, $[\eta]$ can be treated as an additional adjustable parameter. Fig. 1 portrays the general features of the present approach in terms of the parameter γ, which dominates the deviation of the viscometric behavior of the mixture from Arrhenius' additivity law in most cases.

In order to visualize the physical meaning of positive or

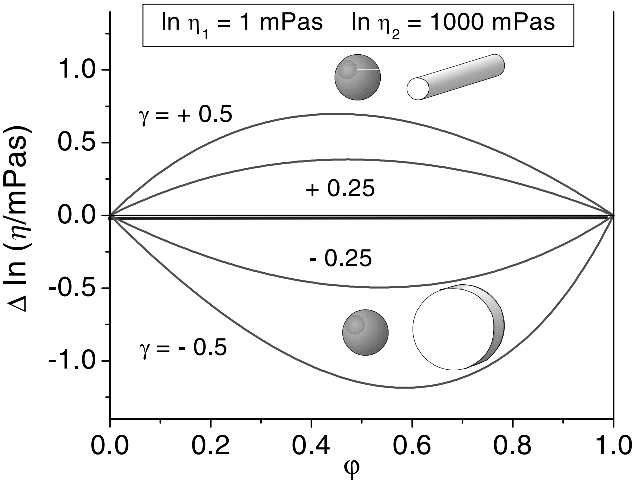


Fig. 1. Model calculations by means of Eq. (2) for $\delta = 6.91$ and the different indicated γ values, setting $\alpha = \lambda = 0$. For $\gamma > 0$ the surface of a polymer segment (identical in its volume with the molar volume of the solvent) is larger than the surface of the solvent. The opposite holds true for $\gamma < 0$. In the case of $\gamma = 0$ surface and volume fractions become identical and $\Delta\ln\eta = 0$.

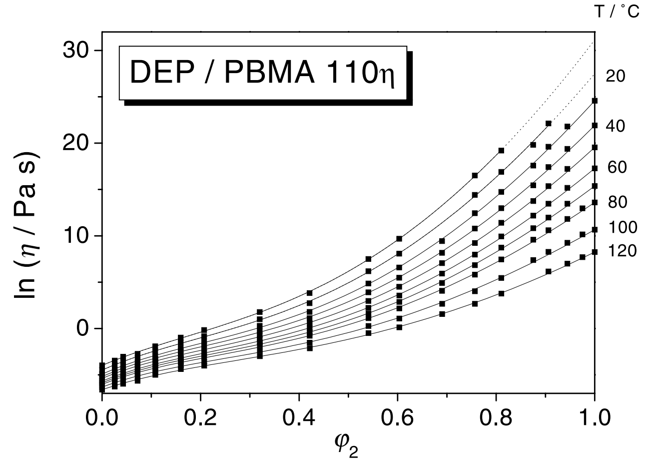


Fig. 2. Zero shear viscosity for the system DEP/PBMA as a function of the volume fraction φ_2 of the polymer at the indicated temperatures. The number after the abbreviation of the polymer states its viscosity average molar mass in kg/mol. The lines are calculated according to Eq. (2).

negative γ values, Fig. 1 shows some calculated excess viscosities for a 1000-fold viscosity of the polymer as compared with the solvent, setting $\alpha = \lambda = 0$. This graph also contains two cartoons visualizing the situation for the simplified case that γ is exclusively determined by the molecular geometries of the components. For these sketches, we assume that the solvent molecules can be represented by spheres and polymer segments by cylinders. A discussion in terms of the segments instead of molecules is permissible for negligible end group effects, given that the surface/volume ratios of the entire polymer molecules and of individual segments become identical. Since the solvent and segment have by definition identical volumes, it is under the present assumptions that the particular chemical architecture of the polymer determines the diameter of the segment and as a result its surface also. Positive γ values result for large solvent molecules like decalin in combination with 'thin' molecules, like polyethylene. Negative γ values are typical for tiny solvent molecules and polymers with backbones that are densely covered by side groups.

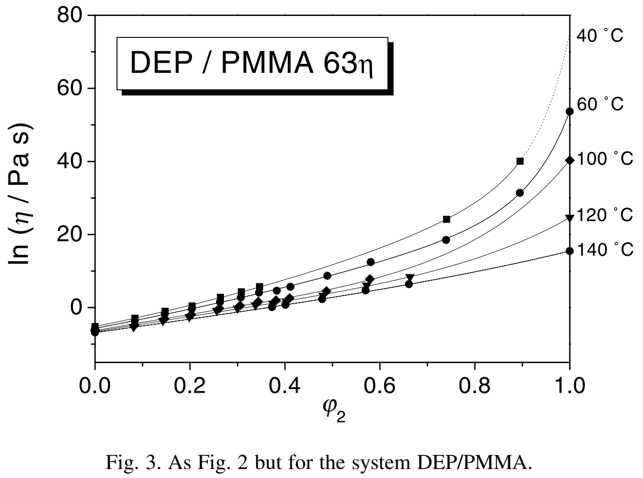


Fig. 3. As Fig. 2 but for the system DEP/PMMA.

3. Primary data and their evaluation

The present considerations use experimental information on the binary systems DEP/PBMA [15] and DEP/PMMA [16] (DEP: diethylphtalate, PBMA: poly(butyl methacrylate), PMMA: poly(methyl methacrylate)). For the discussion of the results obtained with these solutions we include the outcome of a previous study [13] on the systems DEP/PM(A) and DEP/PVAc (PM(A): poly(methyl acrylate), PVAc: poly(vinyl acetate)). This choice enables a determination of the role of molecular architectures of the different polymers, since the solvent was in all cases DEP because of its low volatility.

Fig. 2 demonstrates how the natural logarithm of the zero shear viscosity η varies with the volume fraction φ of PBMA at different temperatures. An analogous representation of the data for the system DEP/PMMA is shown in Fig. 3. At the lowest measuring temperatures the solutions solidify before the solvent content falls to zero in both cases. Under these conditions the viscosities of the pure polymers were determined by treating η_2 as an additional adjustable parameter. How the excess viscosities (cf. Eq. (2)) vary with composition can be seen from Figs. 4 and 5. These curves are calculated setting $\lambda = 0$ and adjusting γ, α plus $[\eta]$. The fitted intrinsic viscosities lie within the expected ranges. That of PBMA in DEP increase approximately linearly from 19 ml/g at 120°C to ca. 22 ml/g at 15°C. The corresponding data for PMMA scatter around 20 ml/g at all temperatures. How γ and α depend on temperature and how they interrelate will be discussed in Section 4.

Figs. 2 and 3 make obvious that the deviations from Arrhenius' mixing law are almost exclusively negative and the more so when T becomes lower. These temperature influences are identical with those observed for the systems DEP/PM(A) and DEP/PVAc. A change in sign of $\Delta \ln \eta$ from positive to negative at low polymer concentrations noted for PM(A) and PVAc is, however, absent for PBMA and PMMA, disregarding a vague indication of

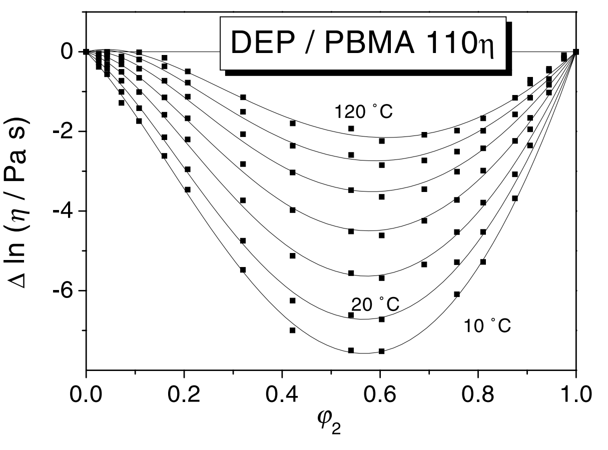


Fig. 4. Excess viscosity for the system DEP/PBMA as a function of temperature at the indicated temperatures. The lines are calculated according to Eq. (2) setting $\lambda = 0$.

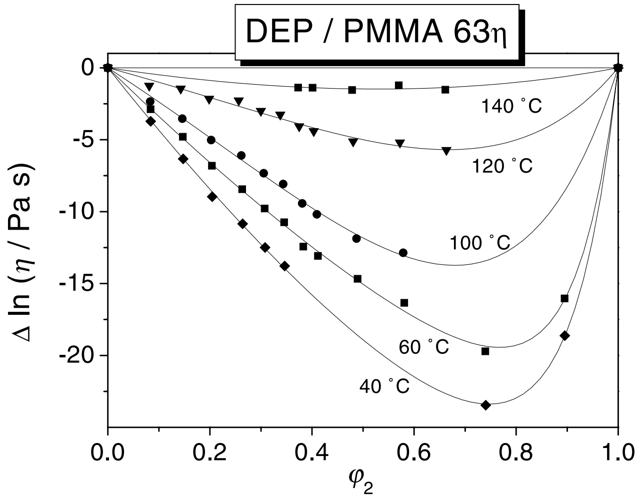


Fig. 5. As Fig. 4 but for the system DEP/PMMA.

such a behavior for the former polymer at the highest temperature.

4. Discussion

According to the literature reports of extensive viscometric data on the solutions of four chemically very similar polymers in the same solvent DEP, we can determine how the structure of the macromolecules influences the characteristic parameters γ and α. Table 1 shows the chemical formulae of the different monomeric units and demonstrates that PBMA and PMMA differ only in the length of the ester group, whereas PVAc and PM(A) contain the same atoms but in a different arrangement. Furthermore, this table contains information on γ_B, the values of the geometrical factor calculated from the molecular architecture of the components by means of group contributions according to Bondi [14] and g_{12}^{SPT}, the integral Flory–Huggins interaction parameter, resulting from the solubility parameter theory [17]. Also stated are the numbers of entanglements E, existing in the melts of the pure polymers calculated from the relation

$$E = \frac{M}{M_e} - 1 \qquad (6)$$

where M_e stands for the entanglement molecular weights (cf. Table 2).

How the variation of γ and α with M and T is the subject of the first part of the discussion. The second part deals with the possibilities to obtain information on the viscosity of the pure polymers at temperatures below T_g from the known composition dependence of η at constant $T < T_g$ at lower polymer contents.

4.1. Characteristic parameters

The variation of γ, the prime parameter of Eq. (2) describing the excess viscosity of mixtures, with temperature is shown in Fig. 6. This graph demonstrates that a naive interpretation of γ as a purely geometric term is not permissible; γ should neither depend on T nor on M. According to the present results and earlier observations, γ decreases as T is lowered and rises with M. The reason for the former behavior is yet unclear. One could think of a temperature dependence of accessibility of molecular surfaces. The latter effect has been interpreted in terms of entanglements leading to additional friction and thus pretending larger surfaces. The different molar masses of the polymers and their corresponding entanglement molecular weights impede a direct comparison of γ for the different polymers

Table 1

Chemical formulae of the different polymers and the number of entanglements E in their melts (for the entanglement molecular weight, cf. Table 2). Also included are some parameters referring to their solutions in DEP: γ_B are the geometrical parameters calculated from the tabulated increments of Bondi [14] and g_{12}^{SPT} is the integral Flory–Huggins interaction parameters resulting from the solubility parameter theory [17]. The large differences between the isomers result from the differences in the densities of PVAc and PM(A)

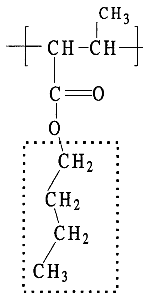
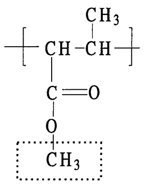
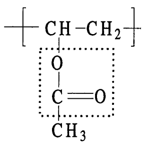
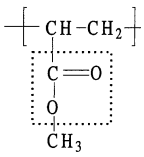
	PBMA	PMMA	PVAc	PM(A)
				
E	3	5–12	10	14
γ_B	− 0.139	0.07	0.185	0.185
g_{12}^{SPT}	0.411	0.092	0.075	0.018

Table 2
Viscosity average molar masses of the polymers M_η, entanglement molecular masses M_e, glass transition temperatures T_g, viscosities of the melts at this temperature and c_1 c_2, the product of the parameters of the WLF equation that does not depend on the reference temperature [20]

	M_η (kg/mol^{-1})	M_e (kg/mol^{-1})	T_g (°C)	Log(η_{Tg} (Pa s)	c_1c_2 (K)
PBMA	110 [15]	27.7	20–27	11.1	3100
PMMA	63 [16]	4.7–10,0	105	15.5	1800
PVAc	100 [21]	9.1	27	14.9	1800
PM(A)	130 [22]	8.8	3	15.9	800

with the theoretically calculated γ_B values. For the present results the effects of different numbers of entanglements become immediately obvious for the isomers, PVAc and PM(A), where γ is considerably larger for the latter polymer due to larger E values. With respect to glass transition, it appears worthwhile to note that γ decreases upon a reduction of T, as the distance to the glass transition temperature becomes smaller, in all cases studied so far.

The temperature dependence of the viscometric interaction parameter α is depicted in Fig. 7. According to the definition, α quantifies the deviation of η_{12}, the (concentration independent) friction between components 1 and 2, from the geometric average of η_{11} and η_{22} (the corresponding data of the pure components). For all polymer/solvent systems evaluated with respect to the parameter α results in negative values. This observation can be tentatively interpreted by the fact that entanglements that are very operative in the absence of solvent lose importance upon a reduction of polymer concentration; the viscosity of the mixture is less than expected because of this reduction in entanglement density at higher dilution and α becomes negative. Like γ the viscometric interaction parameter falls upon an approach of T_g.

According to these considerations γ as well as α should depend strongly on E, the number of entanglements in the melt. These two parameters should, therefore, not be independent of each other. Indeed such an interrelation were already observed in the past [13]. Fig. 8 shows this situation for the present system in terms of γ as a function of α. The observation that the dependence for PBMA ($E = 3$) exhibits the lowest slope, followed by PVAc ($E = 10$) and PM(A) ($E = 14$) corroborates the tentative explanations concerning the role of entanglements.

4.2. Melt viscosities below T_g

It is a well established fact that the viscosity of a polymer melt does not become infinitely large at T_g, despite the freezing of the slowest molecular motions. This feature is for example clearly demonstrated by the creep experiments reported in the early work of Bueche [16]. The viscosity as a function of T is often described by the WLF relation [18]

$$\log\frac{\eta}{\eta_0} = -\frac{c_1(T - T_0)}{c_2 + (T - T_0)} \tag{7}$$

where the reference temperature and the corresponding viscosity are indicated by the subscript 0 and c_1, c_2 are system-specific parameters. One possibility to estimate viscosities below T_g rests on an extrapolation of dependencies $\eta(T)$, measured for the pure melt ($\varphi = 1$) to $T < T_g$ according to relation (7). In the context of the present work we ask whether an extrapolation of $\eta(\varphi)$ measured for solutions of the polymer under consideration at constant $T < T_g$ to vanishing solvent content by means of Eq. (2) yields the

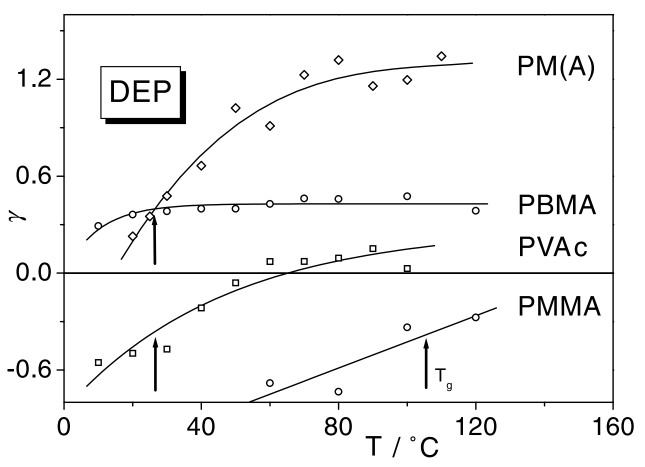


Fig. 6. Temperature dependence of the geometric factor γ for the different systems. The arrows indicate T_g.

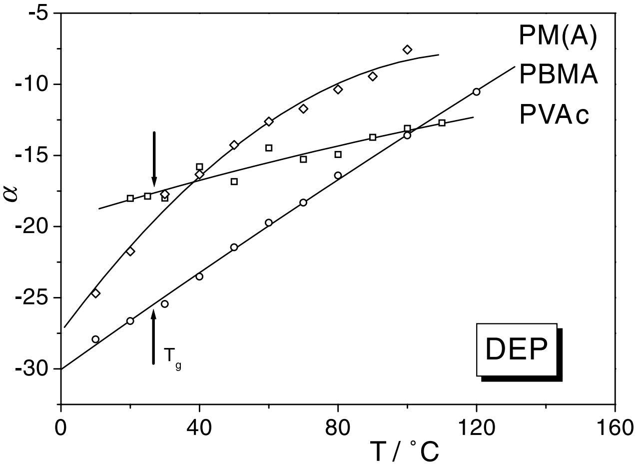


Fig. 7. Like Fig. 6 but for the viscometric interaction parameter α. The information for PMMA is missing, since the number and precision of the primary data lead to large scattering. All points for that polymer are located below the different curves.

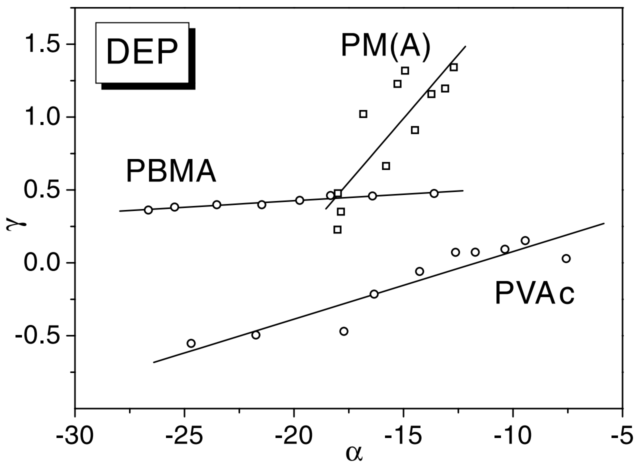


Fig. 8. Interdependence of the geometric factor γ and the viscometric interaction parameter α for the different systems.

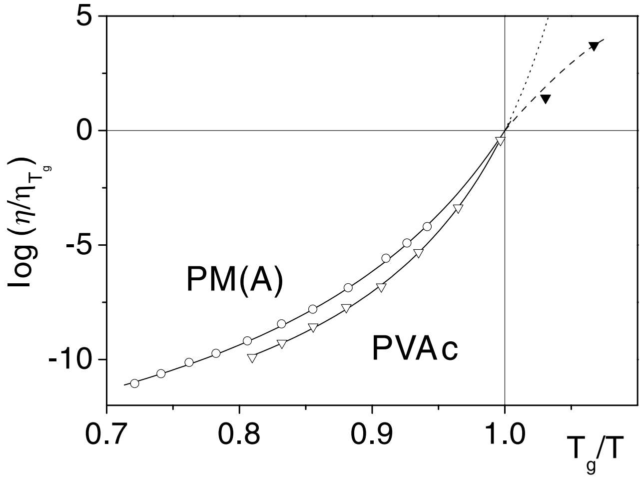


Fig. 10. As Fig. 9 but for the PVAc and PM(A), the polymeric isomers.

same results. The data required for this discussion are collected in Table 2. In Fig. 9 we compare the solidification of PBMA and PMMA, the polymers differing only in the length of their side chains, and of PVAc and PM(A), the isomeric polymers, in Fig. 10. According to the present results, PBMA and PMMA (Fig. 9) behave fundamentally different. The most outstanding feature is the lower viscosity of the former polymer under comparable conditions. This difference, amounting to four orders of magnitude at T_g (Table 2), results from the high mobility of the butyl side groups. The data extrapolated for PBMA from the concentration dependence match the prediction of the WLF equation very well, whereas the viscosity of PMMA rises as T falls below T_g much less than predicted. The discrepancy can reach many orders of magnitude at the lowest temperatures, where the results of creep experiments with the pure PMMA (open circles) and that extrapolated from solution (filled circle) agree almost perfectly. According to this result, the viscosities of PMMA and PBMA glasses tend to approach each other at very low temperatures. Presently, it is unclear how reliable and how general this result is. Two observations are, however, in favor of the assumption that the effects are real: (i) experiments on the dye probe diffusion of PMMA below the glass transition temperature [19] that yielded diffusion coefficients exhibiting the same trend as the present rheological data (cf. Fig. 8 of Ref. [19]) and (ii) the results for PVAc shown in Fig. 10. In the reduced presentation of this graph, the temperature dependencies of η is very similar for the two isomeric polymers. Melt viscosities below T_g were neither stated for PM(A) nor for PVAc. In the latter case, however, the concentration dependence of the viscosity of the solutions was reported for $T < T_g$ so that an extrapolation is possible. Like with PMMA, these data are situated well below the prediction of the WLF relation. One might, therefore, speculate that mobility of polymer chains below T_g might be considerably higher than expected in terms of generally accepted theoretical concepts.

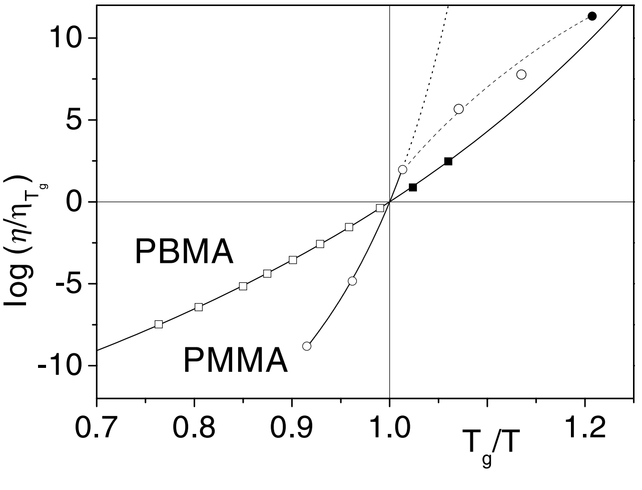


Fig. 9. Reduced Arrhenius plot for PBMA and PMMA, the esters of different lengths of the side groups. The full lines are calculated according to Eq. (7); for PMMA the continuation into the glassy state is dotted. Open symbols represent measurements, full symbols refer to values extrapolated from solution data.

5. Conclusions

Data published on the viscosities of solutions of polymers that are glasses at the measuring temperatures were evaluated with respect to the applicability of an approach based on surface fractions as concentration variables. The results demonstrate that the method is well capable to include this special situation of great practical interest without modifications of the concept. The two central parameters characterizing the polymer/solvent systems obtained in the course of these evaluations become smaller as T is lowered. In view of the previously observed molecular weight influences this observation is against intuition. One would have expected that the entanglements, undoubtedly governing $\gamma(M)$ and $\alpha(M)$, become more efficient upon a reduction of T. This finding still lacks a convincing explanation and requires well-directed additional experiments.

Another interesting feature consists in the possibility to extrapolate the viscosities measured for the polymer solutions in an unambiguous manner to vanishing solvent content, i.e. obtain information on the viscosities of pure polymers below their glass transition temperature that is otherwise difficult to obtain. The present results indicate that the WLF relation describes the increase of viscosity upon a reduction of T at $T < T_g$ accurately only for polymers with comparatively low viscosities at T_g like PBMA. For PMMA and PVAc these values are almost four orders of magnitude higher than that extrapolated from solution data and, in the case of PMMA, than measured in creep experiments. These results are backed by experiments on the dye probe diffusion in PMMA below the glass transition temperature [19] and deserve further investigation.

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