

PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Solubility of Polymethyl Methacrylate in Organic Solvents

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Received June 7, 2005

Abstract—Solubility of polymethyl methacrylate in 12 organic solvents at 30–70°C was studied.

The resistance of polymers to organic solvents is theoretically and practically important. At the same time, studies in this area are mainly concerned with swelling of polymers in various media. The dissolution process itself, despite its wide application in various technologies, has been studied to a considerably lesser extent.

According to the Nernst diffusion theory, the dissolution of low-molecular compounds in liquids occurs at the phase boundary rapidly and is limited by diffusion of components toward and away from the surface of a solid. The process rate v is determined by the diffusion coefficient D , boundary layer thickness l , and difference of the solute concentrations in the surface layer (c_0) and in the bulk (c):

$$v = \frac{D}{l}(c - c_0). \quad (1)$$

However, the process is considerably more complex in the case of polymers. Here, mention should be primarily made of studies by Ueberreiter *et al.* [1–4], who established for the example of polystyrene that the dissolution of a polymer is preceded by its swelling, with the subsequent formation of caoutchouc-like layer on the surface. Also, it was suggested that the overall rate of the process is determined by the rate of diffusion of a liquid into the polymer, in accordance with second Fick's law. It was found in [4] that the dissolution rate of polystyrene steadily decreases in the series of alkyl acetates as their molecular weight increases. However, attempts to relate the experimentally determined rate of polystyrene dissolution to the Einstein–Stokes coefficients

$$D = kT/6\pi\eta r \quad (2)$$

(D is the diffusion coefficient; η , viscosity; and r , radius of a solvent molecule) failed. This result is not surprising because no satisfactory correlation has been found until recently between the amount of adsorbed liquid S or the swelling rate and the physicochemical characteristics of solvents even for the first presumed stage of the dissolution, i.e., for swelling. The generally accepted Flory–Huggins theory, based on the Hildebrandt model of regular solutions, yields only semiquantitative relations and requires that an empirical correction interaction coefficient should be used [5]. Attempts to relate S to the electrophilicity E_T of solvents by Reichardt [6], their molal volume V_M [7], etc. have been no successful either.

At the same time, it was established in [8] that the only relationship between the limiting viscosity number of a polymer and the degree of its equilibrium swelling is that they behave in a similar way [8].

It was assumed that different types of interactions are involved in swelling of polymers and diffusion of solvents in these materials [9, 10]. Therefore, to obtain an adequate relation between S or D and solvent characteristics, it is necessary to take into account, in accordance with the linear free energies (LFE) principle, all mutually independent changes in the Gibbs energy of the components, associated with these parameters: $\Delta G = \sum \Delta g_i$.

To reveal the possible correlation between the physicochemical characteristics of organic solvents and the rate of polymer dissolution in them, we studied the dissolution of polymethyl methacrylate (PMMA) samples with an average molecular weight of 139 000 in 12 organic solvents. The dissolution rates at 30, 40, 50, and 70°C were determined gravimetrically.

Table 1. Degree Q of PMMA dissolution in organic solvents at 30°C

Solvent	Q , wt %, at indicated time, min							
	10	20	30	40	50	60	90	120
Benzene	10.4	18.9	25.2	29.2	34.7	38.6	49.9	68.5
Toluene	5.2	11.8	15.5	18.7	21.4	23.1	29.7	40.0
<i>o</i> -Xylene	3.1	4.9	6.1	7.3	8.7	9.2	11.3	15.5
<i>m</i> -Xylene	11.8	13.5	14.6	16.7	17.8	19.5	26.2	27.3
Trichloromethane	0.3	1.1	1.2	1.4	1.8	2.0	3.4	4.0
Trichloroethylene	35.8	65.7	88.4	96.0	–	–	–	–
1,4-Dioxane	5.3	10.6	14.4	17.2	19.7	21.6	27.2	37.9
Cyclohexanone	13.6	24.6	31.7	45.2	53.1	65.0	73.2	77.3
Acetophenone	8.0	14.0	18.1	21.0	23.1	25.8	31.9	45.6
Ethyl acetate	19.7	36.6	48.1	56.7	64.3	71.9	89.5	–
Pentyl acetate	2.2	3.2	4.5	4.8	5.4	6.1	7.2	8.5
Dimethylformamide	6.7	18.7	26.1	33.4	38.7	45.8	61.8	84.7

Table 2. Dissolution of PMMA samples in organic solvents at different temperatures

Solvent	Q , wt %, at indicated time, min														
	10			20			30			40			60		
	40°C	50°C	70°C	40°C	50°C	70°C	40°C	50°C	70°C	40°C	50°C	70°C	40°C	50°C	70°C
Benzene	24.4	33.3	47.8	38.1	57.3	90.3	60.0	77.6	–	73.0	90.7	–	88.9	–	–
Toluene	14.1	29.8	51.0	23.9	49.1	96.8	39.7	65.3	–	50.4	75.5	–	61.5	97.0	–
<i>o</i> -Xylene	5.0	13.5	24.6	6.8	22.3	50.4	13.6	26.2	58.7	19.1	31.4	80.0	23.6	47.6	–
<i>m</i> -Xylene	3.9	10.3	12.2	8.0	25.2	41.9	10.1	39.8	66.0	15.4	54.0	85.0	22.2	73.3	–
Trichloromethane	9.5	2.8	5.7	11.5	9.7	11.4	12.6	12.3	29.5	14.2	25.8	42.0	16.7	33.9	63.0
1,4-Dioxane	11.5	18.7	31.9	18.3	39.6	74.0	31.1	55.1	93.8	44.0	72.8	97.8	60.0	96.8	–
Cyclohexanone	5.7	23.0	16.9	10.1	54.5	36.2	13.0	59.1	56.4	19.7	71.4	67.0	30.6	85.1	97.2
Acetophenone	13.3	21.3	45.9	14.0	28.5	34.3	43.7	53.9	96.9	53.4	65.9	–	69.6	94.6	–
Ethyl acetate	18.8	37.0	36.9	39.8	62.6	87.6	57.0	80.8	–	76.4	–	–	98.3	–	–
Pentyl acetate	4.6	8.5	7.7	9.5	26.9	27.3	12.5	41.9	42.7	17.6	54.2	66.8	26.9	74.1	82.3
Dimethylformamide	12.5	19.6	35.1	25.2	28.1	66.8	35.8	48.5	96.6	56.0	67.9	–	75.0	–	–

The experimental results obtained are listed in Tables 1, 2. The data on the dissolution rate of PMMA at 30°C are analyzed in most detail (Table 1). As can be seen, there is no direct correlation between the dissolution rate and the structure or properties of a solvent, including its polarity. The best solvents for PMMA are partly substituted hydrocarbons, trichloromethane and trichloroethylene, in which polymer samples dissolve virtually completely in 30 min. At the same time, they nearly do not dissolve at all in trichloromethane. Good solvents are polar ethyl

acetate and cyclohexanone. However, their ability to dissolve PMMA considerably decreases, as the molecular weight of esters increases, in agreement with the data of [4], and an even more polar dimethylformamide (DMF) dissolves PMMA even more slowly. Moreover, a strong difference in the dissolving power is even observed between aromatic hydrocarbons. At the same time, the curves describing the relative rate of the loss of mass by samples in the course of time, $Q = (w_0 - w_\tau)/w_0$, where w_0 is the initial mass of the sample and w_τ , its mass at an instant of time τ , are

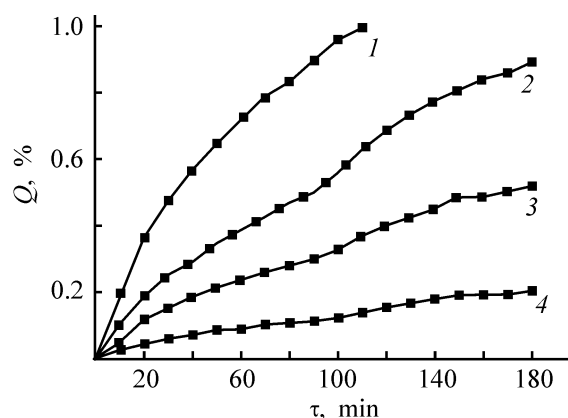


Fig. 1. Relative loss of mass by PMMA samples Q vs. time τ at 30°C in (1) ethyl acetate, (2) benzene, (3) toluene, and (4) *o*-xylene.

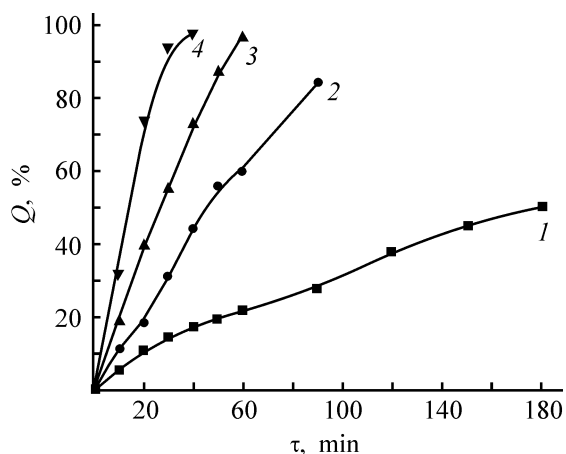


Fig. 2. Degree Q of PMMA dissolution in 1,4-dioxane vs. time τ . Temperature (°C): (1) 30, (2) 40, (3) 50, and (4) 70.

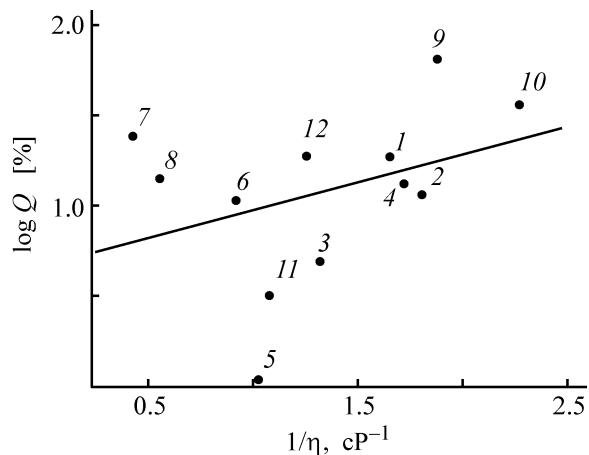


Fig. 3. Relationship between the degree Q of polymer dissolution in various solvents and their viscosity η (30°C, 20 min). (1) Benzene, (2) toluene, (3) *o*-xylene, (4) *m*-xylene, (5) trichloromethane, (6) 1,4-dioxane, (7) cyclohexanone, (8) acetophenone, (9) trichloroethylene, (10) ethyl acetate, (11) pentyl acetate, and (12) dimethylformamide.

always nearly linear, irrespective of the type of a solvent and temperature (Fig. 1).

Similarly to the rate of chemical reactions, the dissolution rate increases, on the average, twofold as the temperature is raised by 10°C (Table 2). A typical example of how the dissolution proceeds in the course of time at different temperatures is shown for dioxane in Fig. 2.

Attempts to describe the process in terms of the Einstein–Stokes dependence were unsuccessful. Figure 3 shows the relationship between the degree of PMMA dissolution (loss of mass in percent at 30°C in 20 min) and the parameter $1/\eta$ of this equation. It can be seen that these quantities exhibit to a certain extent opposite types of behavior: the degree of PMMA dissolution decreases as the solvent viscosity becomes higher, rather than a linear relationship. Especially strong deviations are observed for incompletely substituted hydrocarbons, trichloroethylene and chloroform.

Similar results were obtained for other time intervals (30, 40, and 60 min), with the deviations of experimental points from a straight line increasing with the extent of the process. This is not surprising, because the viscosity of the liquid phase gradually increases as it is saturated with the dissolved polymer. The deviations of the points also markedly increase with the temperature of the experiment, which can be attributed to dissimilar changes in viscosity with temperature for different solvents.

Somewhat better results were obtained with another parameter of the solvent, the molar volume V_M , which is directly related to the molecule radius r in formula (2). It was shown in [11] that the molar volume is an important parameter for generalization of data on the swelling rates for carbons in various solvents, with the process rate decreasing as this parameter becomes larger [11]. Similar results were obtained in the case in question. However, no clearly defined relationship could be obtained, either. Therefore, we attempted to find out whether the values obtained can be quantitatively generalized on the LFE principle by simultaneously taking into account the influence of both parameters in accordance with the dependence:

$$\log Q = a_0 + a_1 \frac{1}{\eta} + a_2 \frac{1}{V_M}, \quad (3)$$

where Q is the relative loss of mass by the PMMA sample (%).

This attempt was unsuccessful too. Thus, the results obtained show that the dissolution kinetics of polymers is a complex process dependent on many

factors. Among them, mention should be made of the opposite directions of the following two processes. The first is the penetration (diffusion) of a solvent into the polymer, which is mainly determined by the size of its molecules. The second is that of a partial dissolution of a gel-like swollen surface layer of the polymer. This process is mainly dependent on the viscosity of the liquid phase, which, in addition, gradually increases in the course of its saturation with the polymer. Apparently, the second process will be also facilitated by agitation of the liquid, which makes its viscosity uniform throughout the polymer volume and prevents formation of highly viscous layers of a polymer solution on the surface of polymers.

Therefore, we attempted to generalize the data on the degree of polymer dissolution at different intervals of time (Tables 1, 2) by using the multiple-parameter Koppel–Palm equation [12], which takes into account different types of solvation, and supplementing this equation with terms that characterize self-association of solvents and their molar volume:

$$\log Q = a_0 + a_1 \frac{n^2 - 1}{n^2 - 2} + a_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_M. \quad (4)$$

Here n and ε are the refractive index and the dielectric constant of solvents, which determine the polarization and polarity and characterize the capacity of the solvents for nonspecific solvation; B and E_T , the Palm basicity and the Reichardt electrophilicity, which determine the specific solvation of the substrate; δ , Hildebrandt solubility, whose square is proportional to the cohesion energy of the medium; and V_M , molar volume of the solvent.

It was found that Eq. (4) adequately describes the dependence of the diffusion coefficients of solvents into the polymer on their physicochemical properties [9, 10]. Indeed, on excluding the most inconsistent data for trichloromethane, the degree of polymer dissolution attained at 30°C in 20 min (Table 1) is satisfactorily described by the following six-parameter equation

$$\log Q = 0.95 + (4.31 \pm 3.54)f(n) + (2.84 \pm 1.91)f(\varepsilon) - (0.95 \pm 0.93) \times 10^{-3}B + (0.088 \pm 0.107)E_T - (5.98 \pm 2.51) \times 10^{-3}\delta^2 - (26.1 \pm 4.32) \times 10^{-3}V_M, \quad (5)$$

$$N = 10, R = 0.987, S = 0.110.$$

On excluding the nonsignificant terms B and E_T , which characterize the specific solvation, we also obtain an adequate four-parameter equation:

$$\log Q = 3.35 + (4.11 \pm 1.48)f(n) + (4.41 \pm 0.63)f(\varepsilon) - (5.31 \pm 0.79) \times 10^{-3}\delta^2 - (26.2 \pm 2.59) \times 10^{-3}V_M, \quad (6)$$

$$R = 0.978, S = 0.109.$$

The above consideration shows that an increase in the size of solvent molecules (V_M) and in their self-association (δ^2) decelerates the dissolution of polymer in the solvents, which is presumably due to the hindrance to solvent diffusion into the polymer. At the same time, the nonspecific solvation of the chains of a polymer by the solvent favors its dissolution. However, particular interesting in this case is the conclusion that the possible specific solvation of PMMA is unimportant for the dissolution process, despite the presence of electron-donating carbonyl groups in its structure. Possibly, this is due to the fact that we studied nearly exclusively typical electron-donating solvents, and the electron-accepting trichloromethane is so active a solvent that it cannot be involved in the comparison.

It should be noted that Eq. (4) yields satisfactory results only for temperatures close to room temperature. Apparently, the effect of polymer diffusion into the liquid, which strongly depends both on the increase in viscosity upon saturation of the solution with the polymer and on the opposite effect of the decrease in the viscosity of the medium on raising the temperature, which is difficult to take into account, will be also the important factors under other conditions.

CONCLUSION

The dissolution rate of polymethyl methacrylate in various organic solvents cannot be described in terms of the Einstein–Stokes dependence. Dissolution is a complex process dependent on the diffusion and solvation phenomena occurring in the system. The maximum dissolution rate is observed in trichloromethane and trichloroethylene. Dissolution in other solvents is determined, on the one hand, by the influence of their polarity and polarizability, which facilitate the process, and, on the other, by the energy density of cohesion and the molar volume, which act in the opposite direction.

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