

Investigations Concerning Dissolution and Swelling of Polymethacrylonitrile in Organic Liquids

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Synopsis

The interaction of various liquids with polymethacrylonitrile (PMCN) was investigated with respect to their ability of acting as solvent or soaking agent. The extent of interaction with the polymer solvents were classified on the basis of the following characteristics—*Category A liquids*: v_A , the rate of dissolution, is determined by v_{rept} , the rate of reptation. A swollen surface layer is formed during dissolution of polymer films. v_A increases with decreasing M_w , the weight average molecular weight. *Category B liquids*: v_A is determined by v_{sol} , the rate of solvation. A swollen surface layer is not formed during dissolution of polymer films. v_A is independent of M_w . *Category C liquids*: They are incapable of dissolving but capable of soaking PMCN. Penetration of polymer films is characterized by features typical of CASE II sorption—a sharp step-wise penetrant profile proceeding with constant velocity v_{orp} . Dissolution and soaking tests with X-ray irradiated PMCN films carried out in category B or C liquids, respectively, revealed the importance of morphological properties regarding the rate of dissolution and sorption, respectively. The observed increase in v_A and v_{orp} with increasing exposure dose was concluded to be due to the radiation-induced increase in free volume rather than to the decrease in M_w .

INTRODUCTION

In recent years the dissolution of glassy linear polymers in organic liquids of low molecular weight has attracted the interest of researchers involved in the development of microelectronic devices with the aid of lithographic techniques such as photo, electron beam, and X-ray lithography. At present, polymers are applied for the generation and replication of fine line structures with line widths down to a few hundred nanometers. In technical processes microstructures are produced in thin polymer films in latent form by irradiation. Subsequent to irradiation the films are treated with a “developer” consisting of a solvent or a mixture of solvent(s) and nonsolvent(s). This way, certain areas of the film are removed and the microstructures develop. A principal obstacle in this “wet developing” procedure concerns swelling of the polymer surface. Commonly, swelling leads to deformation or even destruction of microstructures. Therefore, in technically applicable procedures aiming at the generation of fine line structures, swelling is to be avoided or at least to be strongly suppressed.

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In the course of our investigations concerning the applicability of polymethacrylonitrile (PMCN) in X-ray lithography, dissolution and swelling phenomena were also studied.¹ An interesting result of these studies concerns the finding that the generation of fine line structures is greatly alleviated by preswelling of the irradiated areas of the polymer film.² In this case preswelling consists in the application of a liquid incapable of dissolving but capable of soaking the polymer. During soaking the polymer is converted from the glassy into the relaxed state, from which, with the aid of a strongly interacting liquid, development is readily achieved. This example demonstrates how advantage can be taken out of the fact that polymers can interact with liquids of a different chemical nature in quite different ways. In this article, results of systematic studies regarding swelling and dissolution of polymethacrylonitrile are reported.

INTERACTION OF LOW MOLECULAR WEIGHT LIQUIDS WITH GLASSY LINEAR POLYMERS

General Treatment of Dissolution of Polymers

Commonly, glassy linear polymers are dissolved when brought into contact with appropriate low molecular weight liquids. Thermodynamically, dissolution is possible if ΔG_m , the free energy of mixing,

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

is negative. This condition holds if ΔH_m , the enthalpy of mixing, does not exceed $T\Delta S_m$. Here, it is assumed that ΔS_m , the entropy of mixing, is positive, which applies to most systems. Regarding the dissolution process, it must be pointed out that solvation has to be discriminated from reptation of macromolecules.² *Solvation* applies to the penetration of molecules of the liquid into the rigid polymer matrix and to the relaxation of the matrix from the rigid into the rubbery state when the content of the liquid has attained a certain value. The subsequent *reptation* process involves disentanglement of the coiled macromolecules and eventually their diffusion into the sol phase. Regarding practical applications it is of some importance whether or not a swollen layer at the interphase polymer/sol phase is formed and it appears that this is critically determined by the ratio of the rates of solvation and reptation $v_{\text{solv}}/v_{\text{rept}}$.

Generally, three modes of action can be discriminated with respect to the interaction of low molecular weight liquids with linear polymers: (a) The polymer dissolves in the liquid with a rather high rate and the rate of dissolution is determined by the rate of reptation ($v_{\text{solv}} > v_{\text{rept}}$). In this case, therefore, dissolution involves the formation of a swollen layer at the interface polymer/solution. (b) The polymer dissolves in the liquid with a rather low rate and the rate of dissolution is determined by the rate of solvation ($v_{\text{solv}} < v_{\text{rept}}$). In this case, therefore, a swollen layer at the interface polymer/solution is hardly formed. (c) The polymer is swollen by the liquid but it does not dissolve. According to this classification three categories of liquids can be defined and liquids which do not affect the polymer at all may be attributed to a fourth category D.

General Treatment of Sorption

Liquids of category C comprise weakly interacting compounds. They penetrate the polymer but are incapable of dissolving it and are, therefore, denoted as penetrants. With respect to penetration kinetics it is discriminated between two cases: *Case I*: The diffusion constant of the penetrant remains constant during sorption and its transport within the polymer is "Fickian," i.e., following Fick's law, which can be written for one-dimensional diffusion neglecting changes in the volume as follows

$$\frac{\partial c}{\partial t} = D \left[\frac{\partial^2 c}{\partial x^2} \right] \quad (2)$$

Accordingly, the concentration profile at the interface can be described by the complementary error function³

$$c(x, t) = c_0 \left[1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right] \quad (3)$$

Case I transport implies that the concentration profile moves into the material with a rate given by eq. (4)

$$(\partial c / \partial t)_c = f(D, c)t^{1/2} \quad (4)$$

Also the mass uptake of penetrant will be proportional to $t^{1/2}$. *Case II*: The diffusion constant D of the penetrant increases during sorption. This increase can be of several orders of magnitude. As a consequence, a sharp step-wise penetrant profile is formed which moves inward from the surface with constant velocity. The concentration of penetrant in the gel phase is constant.⁴⁻⁸

EXPERIMENTAL

Synthesis of Polymethacrylonitrile

Methacrylonitrile freed from the stabilizer was polymerized at 60°C with the aid of AIBN. The monomer contained an impurity which could not be separated by distillation. Its removal was achieved, however, by prepolymerization to low conversion with subsequent distillation. Polymers were characterized with respect to molecular weight distribution and weight average molecular weight by gel permeation chromatography and by light scattering measurements, respectively. Details have been reported earlier.² Table I presents a list of the polymethacrylonitrile samples used during this work.

Dissolution and Sorption Tests

Thin polymer films were placed on silicon wafers or glass plates with the aid of spin-coating using cyclohexanone solutions. Remaining solvent traces were removed by baking the films in a vacuum oven for 1 h at 220°C. The thickness of films coated onto glass plates or silicon wafers was measured with

TABLE I
Characterization of Polymer Samples

Sample	Method of preparation*	M_w	M_n
PMCN 108.5	a	1.0×10^5	
PMCN 108.4	a	2.0×10^5	
PMCN 108.3	a	5.0×10^5	
PMCN 101.3	a	1.0×10^6	
PMCN 101.2	a	2.0×10^6	1.2×10^6
PMCN 101.1	a	3.0×10^6	1.5×10^6
PMCN 112.2	a	1.4×10^6	8.4×10^5
PMCN 112.1	a	1.7×10^6	8.9×10^5
PMCN S1.2	a	3.5×10^6	2.0×10^6
PMCN D3	b	2.0×10^5	7.1×10^4
PMCN D4	b	9.1×10^5	1.2×10^5

* a: Fraction of bulk polymerized sample.

b: Unfractionated sample obtained by solution polymerization of monomer purified by pre-polymerization.

the aid of an interference microscope or a profilometer (Alphastep, Tencor Instruments), respectively. After baking, the thickness of the films was about 1 μm .

Dissolution and sorption experiments were performed in the following way: under slight agitation the film was dipped into the thermostated liquid. Subsequently, it was rapidly transferred to a methylpropylketone bath, where it was kept for 30 sec. Afterward, it was dried in an air stream and the thickness was measured. Dissolution processes were always studied to complete dissolution of the film.

Films treated with solvents of category A were swollen at the surface which made them slightly turbid. Moreover, speckled patterns originating from inhomogeneities in the swollen layer were observed with the polarization microscope. In some cases, an increase in film thickness was detected immediately after the film was brought into contact with the solvent. This effect, which was measured with the profilometer, was restricted to solvents of category A and did not occur with solvents of category B.

Irradiation of Films

Silicon wafers coated with PMCN were irradiated with soft X-rays (λ : 0.2 to 1.2 nm) generated by electrons circulating in the electron storage ring BESSY. Details have been reported elsewhere.²

RESULTS

Dissolution Experiments

Phenomenological differences became obvious upon treating PMCN films with liquids of different chemical nature. Most obvious was the formation of a thick swollen surface layer prior to dissolution in certain liquids or mixtures

of liquids. In other liquids swelling was not very significant or not existent. The various observations made during these tests are summarized in Table II. They served as aids in classifying liquids into categories A or B.

Dissolution of PMCN in Liquids of Category A

Typical results obtained with solvents of category A are presented in Figure 1, where it is shown how the thickness of the polymer film decreased with time. Notably, the polymer sample having the lower M_w dissolved more rapidly than the polymer sample of the higher M_w . Moreover, with the high molecular weight sample, dissolution was preceded by an induction period due to swelling. In γ -butyrolactone/*o*-xylene and DMSO/*o*-xylene swelling was clearly indicated by an initial increase in film thickness. These results demonstrate the molecular weight dependence of the dissolution process as far as liquids of category A are concerned.

Dissolution of PMCN in Liquids of Category B

The rate of dissolution was found independent of the molecular weight of the polymer when liquids of category B were employed as solvents. Typical results are presented in Figure 2, where it is shown that $-\Delta d$ increased linearly with time and that both polymer samples dissolved with the same rate in cyclohexanone. Similar results were obtained with other liquids such as cyclopentanone, benzonitrile, and acetophenone. Dissolution rates measured with various PMCN samples in benzonitrile at 15°, 20°, and 25°C are listed in Table

TABLE II
Interaction of Various Liquids at 22°C with PMCN Films, Prebaked Prior
to Solvent Treatment at 220°C for 60 min*

Category	Liquid	Sample	
		PMCN D4	PMCN S 1.2
A	Dimethylsulfoxide	++	++
A	Dimethylsulfoxide/ <i>o</i> -Xylene (50/50, vol./vol.)	++	++
A	γ -Butyrolactone	++	++
A	Acetone		++
A	Methylethylketone		++
A	Acetonitrile		++
A	Dimethylformamide		++
A	γ -Butyrolactone/ <i>o</i> -Xylene (50/50, vol./vol.)	+	+
A	<i>N</i> -Methylpyrrolidone	+	+
A/B	<i>N</i> -Methylpyrrolidone/ <i>o</i> -Xylene (50/50, vol./vol.)	-	+
B	Cyclohexanone	-	-
B	Cyclopentanone	-	-
B	Acetophenone	-	-
B	Benzonitrile	-	-

* Denotations: ++: major swelling of surface during dissolution; +: minor swelling of surface during dissolution; and -: no swelling of surface during dissolution.

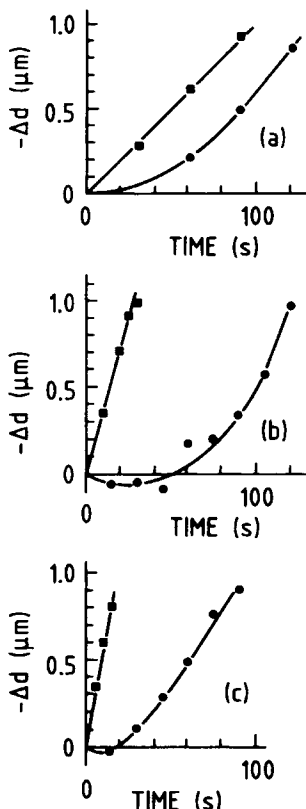


Fig. 1. Dissolution of polymethacrylonitrile in solvents of category A at 22°C. Decrease of film thickness vs. time. (a) *N*-methylpyrrolidone/*o*-xylene (50/50, vol./vol.); (b) γ -butyrolactone/*o*-xylene (50/50, vol./vol.); (c) dimethylsulfoxide/*o*-xylene (50/50, vol./vol.). ●: PMCN S1.2 ($M_w = 3.5 \times 10^6$; $M_n = 2.0 \times 10^6$). ■: PMCN D4 ($M_w = 9.1 \times 10^5$; $M_n = 1.2 \times 10^5$).

III. All these findings are in accordance with the fact that, here, the rate of dissolution was determined by v_{soliv} , the rate of solvation.

Dissolution of X-Ray Irradiated PMCN Films in Liquids of Category B

It has been shown earlier,^{9,10,11} that PMCN undergoes predominantly main-chain scission upon irradiation with ^{60}Co - γ -rays or soft X-rays. The 100 eV-yield of main-chain scission is: $G(S) = 3.3$ to 3.6.

Crosslinking was not detected. Dissolution experiments with X-ray-irradiated PMCN films yielded the following results: The rate of dissolution $v_{A,D}$ increased linearly with D_{exp} , the exposure dose. This can be seen from Figure 3, where the relative dissolution rate is plotted vs. the exposure dose. These results were obtained with PMCN films not treated thermally after irradiation. When, on the other hand, irradiated films were annealed to temperatures above the glass transition temperature ($T > T_g$) prior to dissolution, $v_{A,D}$ was found almost equal to $v_{A,o}$. Accordingly, it can be concluded that the decrease in molecular weight did not affect the dissolution rate. This is in accordance with the results

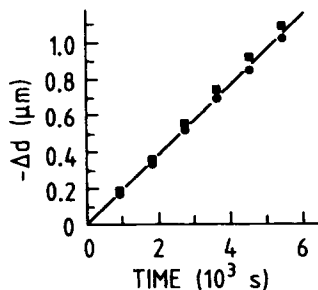


Fig. 2. Dissolution of polymethacrylonitrile in neat cyclohexanone, a solvent of category B, at 22°C. Decrease of film thickness vs. time. ●: PMCN S1.2 ($M_w = 3.5 \times 10^6$; $M_n = 2.0 \times 10^5$). ■: PMCN D4 ($M_w = 9.1 \times 10^5$; $M_n = 1.2 \times 10^5$).

dealt with previously where it was shown that the rate of dissolution is independent of the molecular weight of the polymer. Therefore, it is assumed that the observed significant increase in v_A is due to radiation-induced changes in film morphology rather than to the decrease in M_w caused by main-chain degradation. This point will be elaborated further in the *Discussion Section*.

Sorption Experiments With PMCN

Aliphatic ketones such as methyl ethyl ketone, methyl propyl ketone, and diethyl ketone appeared to be typical representatives of category C liquids. They penetrated PMCN films but were incapable of dissolving the polymer. Upon sorption the films were swollen only slightly, the maximum increase in volume being about 3%. With respect to sorption the important feature applies to the fact that uptake of liquid by the polymer induces a transition from the glassy to the relaxed state.

In order to study the penetration kinetics PMCN films were treated with the penetrant for a certain time and subsequently dissolved in a solvent of category B. It turned out that layers previously soaked with the penetrant dissolved much more rapidly than unsoaked layers. This is shown in Figure 4, where the decrease in film thickness is plotted vs. time. Here, the intersection point of the straight lines indicates the penetration depth of the penetrant. It turned out that the penetration depths obtained this way increased linearly

TABLE III
Rates of Dissolution of PMCN in Benzonitrile

Sample	M_w	v_A (nm/s)		
		15°C	20°C	25°C
PMCN 108.5	1.0×10^5	0.60	1.8	4.1
PMCN 108.4	2.0×10^5	0.65	1.9	4.4
PMCN 108.3	5.0×10^5	0.66	2.0	4.3
PMCN 101.3	1.0×10^6	0.75	2.4	3.4
PMCN 101.2	2.0×10^6	0.61	2.2	3.4

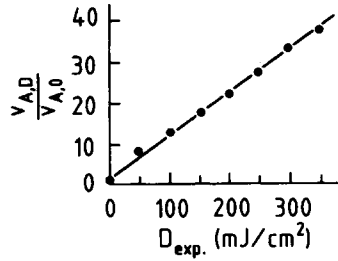


Fig. 3. Dissolution of X-ray irradiated polymethacrylonitrile in cyclohexanone/*o*-xylene/water (63/36/1) at 22°C. Relative rate of dissolution as a function of the absorbed dose. Rate of dissolution of the nonirradiated polymer $v_{A,0} = 0.06$ nm/s.

with soaking time indicating that the penetrant diffused into the film in a sharp front as is expected for Case II sorption. Typical results are shown in Figure 5(a), which also contains results obtained with PMCN samples previously irradiated with X-rays to various doses. Obviously, the sorption rate increased with the exposure dose and it can be inferred from Figure 5(b) that, within the error limits, v_{sorp} is proportional to D_{exp}^2 .

DISCUSSION

Dissolution Experiments

From the results of the dissolution experiments with PMCN it is inferred that the classification of solvents into two categories postulated in the Experimental section is justified. The attribution of solvents to categories A or B on the basis of surface swelling phenomena was supported by the molecular weight dependence of the rate of dissolution v_A . Penetration of solvents of *category A* into PMCN films was accompanied by the formation of a swollen surface layer indicating that v_A is determined by v_{rept} , the rate of reptation. Moreover, the dissolution rate decreased with increasing molecular weight and, at high molecular weight, dissolution was preceded by an induction period during which the volume of the film increased. In the case of solvents of *category B*, on the

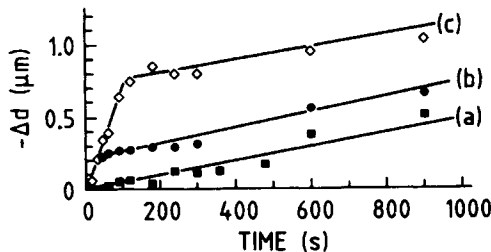


Fig. 4. Dissolution of X-ray irradiated polymethacrylonitrile films (PMCN D4) in cyclohexanone/*o*-xylene/water (63/36/1) at 22°C. $D_{\text{exp}} = 100$ mJ/cm². Decrease of film thickness vs. time for films soaked with methyl propyl ketone prior to dissolution. Soaking period (in min): 0 (a), 60 (b), and 180 (c).

other hand, v_A was found independent of the average molecular weight and the surface layer of polymer films did not swell during dissolution indicating that, here, v_A is determined by v_{soln} , the rate of solvation. Regarding dissolution of PMCN in category B solvents v_A was found to depend on film morphology. This was inferred from the results presented in Figure 3 demonstrating the linear dependence of v_A on the exposure dose. Taking into account that, in this case, v_A is independent of M_w it can be concluded that the increase in v_A with absorbed dose reflects a radiation-induced change in film morphology rather than the decrease in average molecular weight due to main-chain scission. Actually, the formation of gaseous products during the radiolysis of PMCN can give rise to changes in film morphology resulting in an increase in free volume, V_F . It appears feasible to assume proportionality between v_A and V_F for unirradiated and irradiated PMCN, respectively,

$$v_{A,O} = K'V_{F,O} \quad (5)$$

and

$$v_{A,D} = K'(V_{F,O} + V_{F,D}) \quad (6)$$

and, moreover, proportionality between $V_{F,D}$ and D_{exp} , the exposure dose

$$V_{F,D} = K''D_{\text{exp}} \quad (7)$$

Then, one obtains

$$v_{A,D} = K'(V_{F,O} + K''D_{\text{exp}}) \quad (8)$$

Accordingly

$$\frac{v_{A,D}}{v_{A,O}} = \frac{V_{F,O} + V_{F,D}}{V_{F,O}} = 1 + \frac{K''}{V_{F,O}} D_{\text{exp}} \quad (9)$$

The dependence of v_A on film morphology, postulated here, was substantiated by dissolution tests on PMCN films annealed after irradiation to $T > T_g$. After annealing $v_{A,D}$ did not vary markedly from $v_{A,O}$, indicating that additional, radiation-induced free volume was destroyed by the heat treatment.

Soaking Experiments

Case II sorption behavior was evidenced in the soaking experiments performed with liquids of category C. On the basis of the *Case II* concept the dependence of the sorption rate on the square of the exposure dose ($v_{\text{sorp}} \sim D_{\text{exp}}^2$) can be explained, provided v_{sorp} is proportional both to the free volume and the equilibrium concentration of the penetrant in the film

$$v_{\text{sorp}} \sim V_{F,D}[\text{PENETRANT}]_{\text{equil.}} \quad (10)$$

Again, proportionality is assumed between $V_{F,D}$ and D_{exp} [vide ante, eq. (7)]. Furthermore, the driving force for the diffusion of penetrant molecules into still unsoaked regions of the polymer film is proportional to the equilibrium concentration $[\text{PENETRANT}]_{\text{equil.}}$ in the gel layer and this concentration increases with decreasing average molecular weight according to

$$[\text{PENETRANT}]_{\text{equil.}} \sim \frac{1}{M} \quad (11)$$

Since the molecular weight decreases with increasing D_{exp} according to

$$\frac{1}{M} \sim D_{\text{exp}} \quad (12)$$

a D^2 law should hold for the dose dependence of $v_{\text{sorp.}}$.

Lithographic Applications

The results obtained in this work are of direct relevance for the application of liquids as developers for positively working resists in lithographic techniques. Here, the generation of vertical fine line structures of high aspect ratio in the submicrometer range affords that the nonirradiated areas of the resist film remain in the glassy state during development. Strong deformations of fine structures are expected if the nonirradiated areas are also converted to the

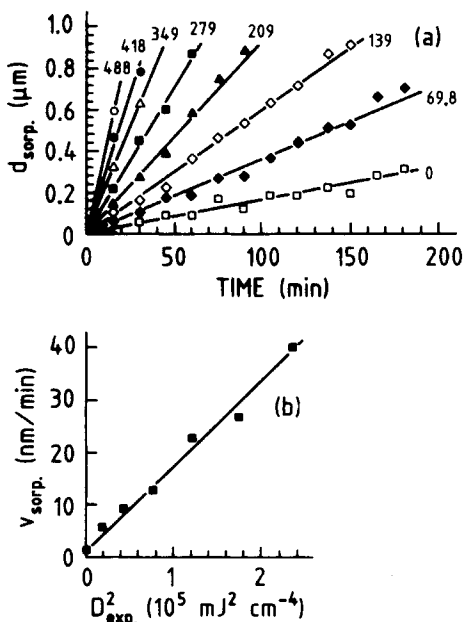


Fig. 5. Penetration of X-ray irradiated polymethacrylonitrile films by methyl propyl ketone at 22°C. (a) Thickness of penetrated layer vs. time at various exposure doses. (b) Penetration rate vs. square of exposure dose.

relaxed state. The difference in solvation rates for irradiated and nonirradiated areas should be maximum in order to achieve optimum contrast values, a situation which can be accomplished provided the dissolution rate is determined by the solvation rate. Consequently, the developer should be a liquid of category B. Finally, it should be pointed out that the difference in solvation rates for irradiated and nonirradiated areas can be strongly enhanced if the nonirradiated areas are penetrated by a category C liquid prior to development; i.e., prior to treatment with a category B liquid.² The significant increase in contrast brought about by this "preswelling" procedure is mainly due to the fact that, in the case of category C liquids, the rate of sorption depends on the exposure dose according to $v_{\text{sorp}} \sim D_{\text{exp}}^2$ (see Fig. 5). As pointed out in the Introduction, details concerning the generation of submicrometer fine line structures in polymethacrylonitrile by X-ray lithography have been dealt with earlier.²

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