An Investigation into the Direct Fluorination Kinetics of Polymeric Membranes

Alexandr P. Kharitonov,*[a] Yurii L. Moskvin,[a] Larisa N. Kharitonova,[a] Alexandr A. Kotenko[b] and Mikhail N. Tulskii[b]

[a] *Institute of Energy Problems of Chemical Physics (Division), Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: egorov@iepcp1.sherna.msk.su*
[b] *Russian Scientific Centre – I. V. Kurchatov Institute, 123182 Moscow, Russian Federation.*

The interference spectroscopy method was used to study the kinetics of fluorinated layer formation on the surface of both optically transparent and non-transparent (composite) polymer membranes based on poly[carbonatesiloxane].

Direct fluorination is a well known method of modifying the gas separation properties of polymer membranes.[1,2] Both gas separation selectivity and productivity (gas permeability) values depend on the polymer fluorinated layer thickness δ_F. The previously described[3] method is suitable only for kinetic investigations of optically transparent polymer films. To investigate non-transparent membranes as well (*e.g.*, composite membranes, *i.e.* membranes consisting of a polymer layer deposited onto non-transparent substrate) we have used the following method. In our experiments we monitored the intensity of the monochromatic light beam (He–Ne laser was used as a light source with wavelength $\lambda = 0.6328$ μm; Hg lamp with filters can also be used) reflected from the membrane surface in the course of the fluorination procedure. The polymer film surface was oriented at an angle α with respect to the incident light beam (this angle can be varied over a 0–45° range; in our experiments usually $\alpha = 45°$). If the untreated and fluorinated polymer layers are separated by a very thin transition (boundary) layer (the thickness of this boundary layer must be much smaller than $\lambda/(4n_F) = 0.1$ μm, where n_F is the refractive index of the fluorinated polymer; n_F is always less than the refractive index for the untreated polymer) and this boundary is parallel to the external surface of the polymer (*i.e.* the fluorinated layer thickness is uniform across the polymer surface), then the intensity of the monitored light shows interference features, *i.e.* the intensity of light depends on time and consists of a series of maxima and minima. The first maximum corresponds to the thickness δ_F of the fluorinated polymer layer $\delta_F = k\lambda/(4n_F)$, where $k = [1 - (\sin\alpha)^2 \cdot (n_F)^{-2}]^{-0.5}$ and α is the angle between the normal to the surface and the direction of propogation of a light beam, the first minimum corresponds to $\delta_F = k\lambda/(2n_F)$ and so on. The interference features of the reflected light beam intensity are due to the interference of two beams reflected from the boundaries of the fluorinated polymer-gaseous phase and the fluorinated polymer-untreated polymer phase. The minimum detectable value of the fluorinated layer thickness is $\delta_F = 0.1$ μm; the upper limit of δ_F is greater than 50 μm.

The above-mentioned method was used to investigate the dependence of the fluorinated layer thickness on time and on fluorine, oxygen and nitrogen partial pressures in the course of fluorination of homogeneous (optically transparent) and composite (non-transparent) membranes based on poly[carbonatesiloxane] (Carbosil^R). Samples sizes were less than 5×5 mm^2. The amount of admixture in the fluorine was less than 0.1 volume % and in O_2 and N_2 less than 0.01%. Fluorination was carried out in a closed metal vessel (volume 300 cm^3). Fluorine consumption in all the experiments was less than 5% so the fluorine partial pressure p_F was considered to be stable. NaF was used as a chemical adsorber of HF, which inhibits the reaction. For Carbosil treated with undiluted fluorine we have measured the n_F value at $\lambda = 0.6328$ μm: $n_F \simeq 1.38$. In a treated polymer all the C–H bonds are substituted for C–F bonds and the polymer becomes totally fluorinated.

The kinetics of the fluorinated layer formation on the surface of homogeneous and composite membranes (treatment conditions: undiluted fluorine, $p_F = 29$–74 Torr and $p_F = 14.7 - 44.1$ Torr, respectively, $T = 296 \pm 2$ K) membranes differs significantly (Fig. 1):

$$\delta_F(\text{homog.}) = 0.43 \times 10^{-3} p_F^{0.81} t^{0.5} + 3.6 \times 10^{-2} p_F^{-0.08} \quad (1)$$

$$\delta_F(\text{compos.}) = 0.45 \times 10^{-3} p_F^{0.93} t^{0.5} + 2.0 \times 10^{-5} p_F^{1.55} t^{1} \quad (2)$$

i.e. δ_F value for homogeneous membranes depends on time as the square root [the second term of equation (1) can be neglected as compared to the first one and its appearance is probably due to a finite fluorine injection time into the reaction vessel] but for composite membranes the main term is proportional to t [the first term of equation (2) can be neglected as compared to the second one when $\delta_F > 0.2$ μm]. It is worth mentioning that the rate of the fluorinated layer formation is much greater for composite membranes than for homogeneous ones (Fig. 1).

We proposed (similarly to ref. 4) that (*a*) the rate of formation of the fluorinated layer thickness is limited by the fluorine gas permeability value P through the fluorinated layer to the untreated layer and (*b*) the relation between the rates of fluorine penetration through the fluorinated layer and chemical reactions (which occur only inside the very thin boundary layer between fluorinated and untreated polymer layers) is as follows: the fluorine pressure decreases linearly to ~ 0 in the vicinity of the above-mentioned boundary when moving from the surface into the polymer bulk. The following equation (3) for the balance of the fluorine flux through the fluorinated layer and the fluorine consumption inside the reaction zone is valid:

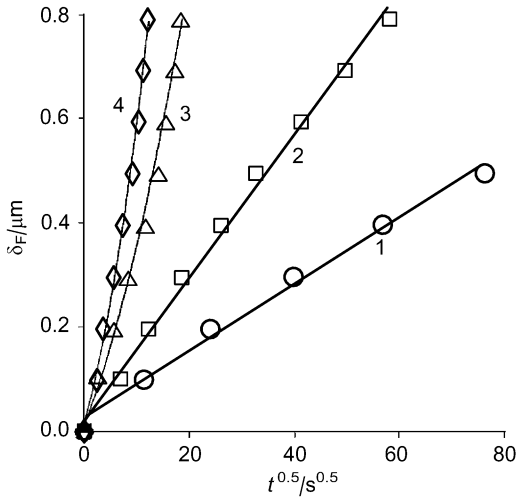

Fig. 1 Fluorinated layer thickness δ_F/μm *vs.* square root of fluorination time t/s. Treatment was carried out with undiluted fluorine at $T = 296 \pm 2$ K. Curves 1 and 2, homogeneous membranes; curves 3 and 4, composite membranes. Curves 1–4 correspond to fluorine partial pressures of 29.4, 73.5, 14.7 and 29.4 Torr, respectively.

$$C \cdot \frac{d\delta_F}{dt} = P \cdot \frac{p_F}{\delta_F} \quad (3)$$

As mentioned above, p_F is constant in the course of treatment and hence equation (4) holds,

$$\delta_F = \left[\frac{2Pp_F t}{C}\right]^{0.5} = (At)^{0.5} \quad (4)$$

where the experimentally determined coefficient C is equal to the quantity of fluorine (cm^3 under normal conditions) consumed to produce 1 cm^3 of fluorinated polymer per 1 cm^3 of fluorinated polymer. [5] The agreement of equations (4) and (1) is evidence that the direct fluorination of homogeneous membranes occurs as described above. Hence, based on the kinetic data [equation (1)] and equation (4) we can calculate the fluorine permeability value P through the fluorinated polymer. [4,5]

The fluorination rate is much greater for composite membranes than for homogeneous ones. This means that the permeability value of the fluorinated composite membrane is much greater as compared to the permeability value of fluorinated homogeneous membranes. In the case of composite membranes we proposed that the main "resistance" to the fluorine flux is situated inside the boundary layer between the fluorinated and untreated polymer layers but not inside the fluorinated layer. Hence the fluorine concentration change through the fluorinated layer bulk is small as compared to the fluorine concentration value on the gas phase – fluorinated polymer boundary and equation (3) can be written as follows: $d\delta_F/dt \sim p_F$. In this case $\delta_F \sim t$ [see equation (2) above]. The nature of this behaviour will be studied in the future.

The influence of N_2 on the fluorination kinetics of composite membranes is negligible (with accuracy ~5–10%) even when the N_2 partial pressure is ten times that of fluorine.

Oxygen inhibits the direct fluorination process: treatment of homogeneous membranes with a F_2–O_2 mixture with oxygen mole fraction μ_O equal to 0.048 and 0.136 results in 2.1-fold and three-fold decrease, respectively, in the fluorine permeability P value.

References

1 R. J. Lagow and J. L. Margrave, *Progr. Inorg. Chem.*, 1979, **26**, 162.

2 J. Jagur-Grodzinski, *Progr. Polym. Sci.*, 1992, **17**, 361.

3 A. P. Kharitonov, Yu. L. Moskvin and G. A. Kolpakov, *Vysokomol. Soedin., Ser. A*, 1985, **27**, 658 [*Polym. Sci. USSR (Engl. Transl.)*, 1985, **27**, 739].

4 A. P. Kharitonov, Yu. L. Moskvin and G. A. Kolpakov, *Khim. Fiz.*, 1985, **4**, 538 [*Sov. J. Chem. Phys. (Engl. Transl.)*, 1985, **4**, 877].

5 A. P. Kharitonov and Yu. L. Moskvin, *Tezisy dokladov 2 Respublikanskoi nauchno-tekhnicheskoi konferentsii "Fizika i tekhnologiya tonkoplenochnykh polimernykh sistem" (Proceedings of the Second Republic conference "Physics and technology of thin-film polymer systems")*, Pruzhany, Brest Region, Republic of Belarus, May 1993, p. 41 (in Russian).

Received: Moscow, 16th December 1993
Cambridge, 1st February 1994; Com. 3/07676H