Research of a Membrane's Material by Reversed Gas Chromatography

O. I. ROMANIUK,[1] A. A. TUROVSKIY,[1] N. I. KURECHKO,[1] R. E. PRYSTANSKY,[1] G. E. ZAIKOV,[2] V. G. ZAIKOV[2]

[1] Department of Physical Chemistry and Technology of Combustible Minerals, L. V. Pisarzhevsky Institute of Physical Chemistry, NAS of Ukraine, 3a Nauchnaya St., Lviv, 79053 Ukraine

[2] N. M. Emanuel Institute of Biochemical Physics, RAS, 4 Kosygin St., Moscow, 117334, Russia

ABSTRACT: Research of a membrane's polymeric material obtained by photoinitiated radical polymerization of oligocarbonate methacrylate and butyl methacrylate (BMA) was conducted by the method of reversed gas chromatography. The presence of defects of two types in the polymer was confirmed: as gaps between grains, and spongy interlayers. It has been established, that the relative size of gaps between grains more than in 1.5 times exceeds the size of interlayers between grains. The selective separation of substances proceeds through interlayers between grains. The size of interlayers (polymer's T_g) depends on structure of an initial composition. Increase of the BMA contents in an initial composition leads to polymer's T_g increase, condensation of interlayers between grains, and increase of selectivity of the appropriate membrane. This dependence has an extremal character. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2725–2728, 2002

Key words: membranes; chromatography; structure; diffusion

INTRODUCTION

The development of scientific bases of polymeric membranes formation by a method of photopolymerization enables creation of new highly effective membranes stable to atmospheric and chemical influences, which can be used for separation of chemical substances, clearing, and desalination of waste water.

The formation of polymeric membranes by photoinitiated radical polymerization from oligomers, already having definite structure, allows synthesization of polymers of a net-type structure with a set of pores, which can be adjusted during polymerization. There is a close relation between the structure of a membrane and its selectivity;

therefore, research of a membrane's material is important at a choice of optimal composition and polymerization conditions. The method of reversed gas chromatography was used for the first time for study of membrane's structure. Research of a material (which membranes were made of) were carried out on a gas chromatograph "Khrom-5" with the detector on heat conduction at temperatures of 300–400 K. Carrying gas was helium. Columns of 3 m length and diameter of 0.3 cm were used. Absolute retention volume calculated according to the formula (1).[1]

$$V_g = \frac{273.2 \nu_a (t_r - t_0)}{T_f m} * \frac{P_0 - p_{H_2O}}{P_0} * \frac{3(p_1/p_0)^2 - 1}{2(p_1/p_0)^3 - 1}$$

(1)

where t_r and t_0 are the retention time of the sorbate and nonsorbing component; ν_a is the ve-

locity of carrying the gas flow, measured by a foam flowmeter; T_f is the temperature of the flowmeter; m is the weight of a stationary phase in a column; p_1 and p_0 are the column's inlet and outlet pressure; and p_{H2O} is the water vapor pressure at the flowmeter temperature.

A stationary phase of researched polymer formed on the surface of the inert carrier ("Khromaton" N-AW with the grain size of 0.2–0.25 mm). The process was carried out in quartz vessel that inert gas—nitrogen—constantly passed through. A watch glass was placed into a quartz vessel and a solid carrier was placed onto the glass. The top part of the carrier was sprinkled by the initiator dissolved in an absolute ethanol. A solid carrier was mixed and the procedure was repeated until the solution of the initiator was entirely consumed. The solid carrier was dried in a nitrogen atmosphere. Similarly, a composition solution (which is used to form a membrane) was rendered onto the carrier's top. The resulting intermediate was dried in a quartz vessel in the suspended state in a nitrogen atmosphere at irradiation by UV beams during the required time for formation of the membrane from the same composition. Then membrane was carefully washed with ethanol and distilled water and dried at room temperature up to constant weight. The amount of polymer of the stationary phase made was 2.5–3%. The column was filled with the prepared sorbent.

We researched polymers obtained by a photoinitiated radical polymerization of compositions on a basis of oligocarbonate methacrylate [CH_2= $C(CH_3)$—$COOCH_2$—O—$C(O)$—$O]_2R$, where R = —$CH_2CH_2OCH_2CH_2$— (0–76%), butyl acrylate (0–24%), and initiator—di(azopropoxy) acetophenone (1.8%).

The diagrams of n-octane retaining by polymeric phases are given in Figure 1. It is seen that dependence curves of the logarithm of the retention volume of the reciprocal temperature have two inflection points that are designated as T_c and T_c'. We believe that the two inflection points are caused by defreezing of the polymer's segmental motion. Such a two-step transition of the net-type polymer from the glass state into an elastic state is, probably, associated to the presence of hole areas of both types. First, the process of defreezing of the segmental motion begins in wide gaps between grains and then, at a higher temperature, spreads on the hole (spongy) material of the interlayers. These two transitions match up to two inflection points, which are designated as
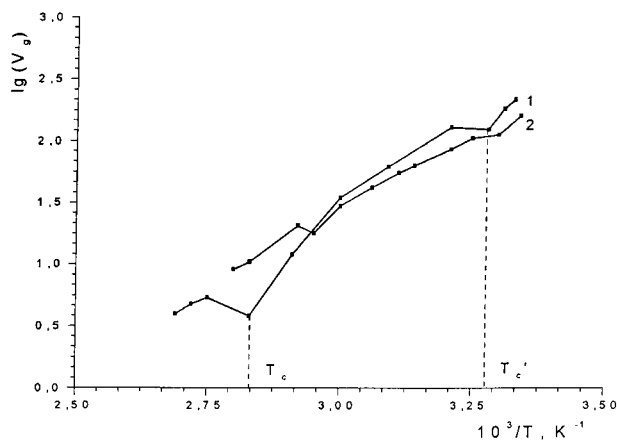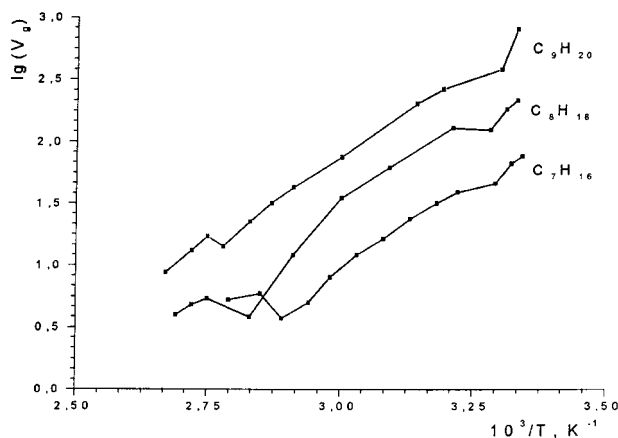

Figure 1 Dependence of the logarithm of retention volume of reciprocal temperature at use of octane as a model for polymers: 1-OKM-2-88%, BMA-12%; 2-OKM-2-76%, BMA-24%.

T_c' and T_c, respectively. This correlates to the theory of reversed gas chromatography,[2] and does not contradict the microheterogeneous theory of net-type polymers, which provides the existence of defects of a supermolecular level such as the hole material of the interlayers and gaps between grains, which are formed at deep polymerization stages.[3] Probably the transfer of the substance through the membrane is carried out through so-called "defective zones," and their specific volume and size in the polymer is related to the membrane's efficiency and selectivity.

The ratio of the gap's sizes between grains and interlayers was investigated. For this purpose the dependence of the T_c' and T_c of the size of the model molecules (n-heptane, n-octane, and n-nonane) was researched. It was found that temperature T_c depends on the length of the molecule (Figs. 2 and 3). The transition to the next homolog, starting with heptane, results in *AN* increase of the virtification temperature T_c on an increment $\Delta T = 7$ K (for polymers containing 12% BMA) (Fig. 2 and Table I), and $\Delta T = 10$ K (for polymers containing 24% BMA) (Fig. 3, Table II). At the same time, T_c' does not change for all ranges of the used models. It is possible to explain that the independence of T_c' of the size of the model molecules to that of the sizes of the gaps between grains are rather big, for the penetration of the model molecules (alkanes C_7–C_9).

According to the diffusion models,[4] the possibility of the model molecule's diffusion in the polymer is realized only when in a polymer's matrix
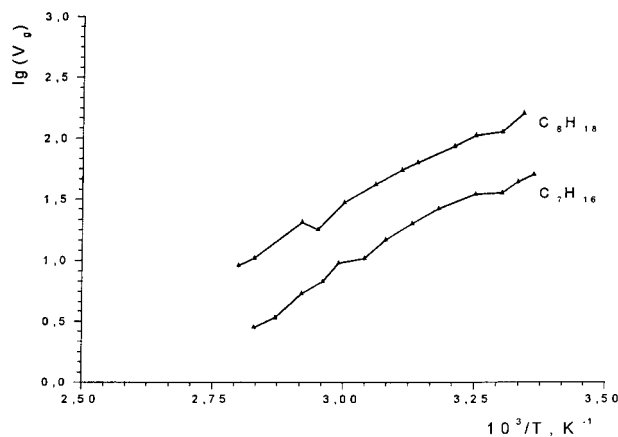
Figure 2 Dependence of the logarithm of retention volume of reciprocal temperature at use of heptane, octane, and nonane as models for polymers OKM-2-88% and BMA-12%.

contains fluctuational holes with dimension (r), in which the molecule of the diffused substance with the length (l) can be placed.

$$r = kl \qquad (2)$$

The increase of T_c at the transition to higher homologs practically means the increase of the size of fluctuational holes (r_0), which are formed at temperature T_c. The holes' size corresponds to the length l_0 of the molecule of that carbon, where the increase of the temperature T_c is observed, because, i.e.:

Figure 3 Dependence of the logarithm of retention volume of reciprocal temperature at use of heptane, octane, and nonane as models for polymers OKM-2-76% and BMA-24%.

Table I   Dependence of Polymer's Vitrification Temperature of Sorbate Molecules' Size

Alkane	T_c'	T_c
12% BMA, OKM-2		
Heptane	304	346
Octane	305	353
Nonane	305	360
24 % BMA, OKM-2		
Heptane	304	329
Octane	304	339

$$r_0 = kl_0 \qquad (3)$$

The size of gaps between grains r' can be related with length l' of the highest alkane, when temperature T_c' did not yet depend on the size of model molecules:

$$r' = kl' \qquad (4)$$

Assuming that coefficient k is a constant for the entire volume of the polymer we have:

$$\frac{r'}{r_0} > \frac{kl'}{kl_0} = \frac{l'}{l_0} \qquad (5)$$

It was established, that the size of gaps between grains exceeds the size of the interlayer between the grains more than 1.5 times.

The influence of the contents of the initial polymeric composition based on OKM-2 on the polymer structure and on the membranes selectivity was investigated. The increase of the BMA contents in the polymer leads to an increase of the

Table II   Dependence of Polymer's Vitrification Temperature, Its Selectivity (R)* and Membranes' Productivity of BMA Content in an Initial Composition Based on OKM-2 $(P = 0.15$ MPa)

BMA Content, %	T_c', K	T_c, K	R, %	Productivity, cm³/cm²/min
0	304	340	15	0.368
8	304	348	31	0.075
12	305	353	70	0.058
24	305	339	22	0.037

Selectivity and productivity was determined at baromembrane separation of an aqueous solution of albumin at the membrane $(p = 0.15$ MPa); concentration was controlled spectrometrically at $\lambda = 540$ nm. $R = (C_0 - C)/C_0 \cdot 100\%$.

membrane's selectivity, which passes through a maximum, i.e., has an extremal character (Table II).

As to vitrification temperature, the first divergence from linearity is observed at the same temperature $T_c' = 304-305$ K, whereas another inflection point T_c— was at different temperatures. An increase of the vitrification temperature at an increase of BMA content in the initial composition passes through a maximum. The highest vitrification temperature corresponds to a membrane of optimal structure and optimal selectivity. Because this vitrification temperature is associated (as was mentioned before) with defreezing of the segmental motion in the interlayers between grains, obviously, the selective separation of the substances is carried out through these interlayers.

REFERENCES

1. Tyukova, I. S.; Tager, A. A.; Morozov, E. V.; Lavrikova, Yu. G. Vysokomolek. Soedin 1990, 32, 2002.
2. Nesterov, A. E. Obrashennaya gazovaya khromatografiya polimerov; Naukova dumka: Kiev, 1988.
3. Berlin, A. A.; Korolev, G. V.; Kaffeli, T. Ya.; Sivergin, Yu. M. Akrilovye oligomery I materialy na ikh osnove; Khimiya: Moscow, 1983.
4. Belousov, V. N.; Kotsev, B, Kh.; Mikitaev, A. K. Doklady AN SSSR 1985 280, 1140.