

Percolation Transition and Conductivity in Macroscopically Anisotropic Two-Component Polymer Membranes

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Synopsis

Percolation conductance has been studied for polypropylene/poly(acrylic acid) membranes (PP-*g*-PAA) prepared by volume grafting of an ionic component onto polypropylene foil. In these membranes the volume fraction of the conducting phase decreases from the surface to the center, bringing some anisotropy into the composition. For this material, the "insulator-to-conductor" transition proceeds at a critical volume fraction V_c equal to 0.395. It has been proved that this critical volume fraction and the critical exponent t , found to be below that predicted by theory, i.e., 1.2 ± 0.03 instead of 1.6 ± 0.2 , result from the gradient in the distribution of the conducting component in the direction of the current flow. Computations of V_c and t for the same PP-*g*-PAA copolymer with a randomly distributed conducting component have led to $V_c^* = 0.08$ and $t^* = 1.53$. A critical exponent t in that range is characteristic of three-dimensional systems; however, V_c is rather low, suggesting a nonspherical shape for the conducting domains.

INTRODUCTION

The percolation theory has been proposed by Broadbent and Hammersley¹⁻³ as a mathematical model for motion through an unpredictable or random medium. The application of percolation theory to the problems of conductance of heterogeneous systems or disordered resistor lattices was presented first by Shante and Kirkpatrick.^{4,5} Recently this theory has been used successfully for the description of conductivity,^{6,7} transport^{8,9} and mechanical¹⁰ properties of some cation selective membranes. In the paper presented here we report on a percolation conductance study of membranes prepared from graft copolymer: poly(propylene-*g*-acrylic acid) (PP-*g*-PAA). Within this copolymer the ion-containing segments aggregate forming clusters embedded in an insulating matrix.^{11,12} This heterogeneous ionic/nonionic system can be considered as a polymer blend composed of conducting [poly(acrylic acid)] and nonconducting (polypropylene) components.

In the previous paper¹³ we proved that, inside the PP-*g*-PAA membranes used here, the fraction of poly(acrylic acid) decreases from the surface to the center causing some ordering of the conducting component within the membrane. Due to this particular structure these membranes can be useful for verifying the applicability of percolation theory to macroscopically anisotropic systems.

Background to Percolation Theory

The percolation theory has been formulated on the ground of percolation probability $P(p)$ in heterogeneous systems or in resistor lattices. In a site percolation model, percolation itself depends on the probability that a conducting center (particle) will occupy a given site in n -dimensional space. In a bond percolation model $P(p)$ is a function of the probability p that two neighbouring lattice nodes will be connected by a conducting bond. At the critical probability point p_c both systems undergo the "insulator-to-conductor" transition. Below p_c the systems behave as insulators whereas above the percolation threshold they behave as conductors. According to the theory, above and near the percolation threshold the dependency of $P(p)$ on p takes the form

$$P(p) \sim (p - p_c)^\beta \quad (1)$$

with β being the critical exponent dependent on the system dimensionality only. On the other hand, p_c depends on the type of percolation considered (i.e., site or bond), the symmetry of the lattice or the spatial distribution of conducting sites, and the dimensionality of a system.

In practice, for conducting systems, the probability p of eq. (1) is often replaced by the concentration of conducting centers or bonds x :

$$\kappa(x) \sim (x - x_c)^t \quad (2)$$

where κ denotes conductivity and t is a universal critical exponent. For three-dimensional systems and a site percolation model, theoretical estimate of t is 1.6 ± 0.2 whereas for a bond percolation model it is 1.5 ± 0.2 .

For the site percolation model, Scher and Zallen¹⁴ proposed the critical volume fraction (CVF) of the conducting phase as a characteristic constant. It can be represented as the product of critical probability p_c and a maximum packing factor (filling factor) f for a given system:

$$V_c = f \cdot p_c \quad (3)$$

Consequently, the conductivity power law takes the form:

$$\kappa = \kappa_0 \cdot (V - V_c)^t \quad (4)$$

where κ_0 is the specific conductivity of a conducting phase. The critical exponent t , like β , depends on space dimensionality only, whereas the V_c is influenced by the mutual disposition and shape of the conducting particles. For the simplest system composed of conducting and nonconducting spheres of radius equal to a half of the lattice spacing, located at lattice nodes, V_c is 0.15 ± 0.02 and depends only slightly on the lattice symmetry.¹⁴ Also, for systems with more complicated topological characteristics and for continuous systems V_c is expected to be the same.^{15,16}

In this paper we present an experimental verification of the applicability of percolation theory to a macroscopically anisotropic system. Taking into

account the fact that in the membranes studied here the CVF can be affected by the state of dispersion and an anisotropy in the disposition of the ionic component we aimed at:

—estimation of CVF for the system with isotropic distribution of the conducting phase in the XY plane and anisotropic in the direction perpendicular to this plane;

—estimation of CVF for the same copolymer PP-*g*-PAA but with an isotropic array of the ionic component;

—verification of the invariability of the critical exponent t .

EXPERIMENTAL

Membranes

Investigations were performed with membranes prepared by volume grafting of acrylic acid onto thin polypropylene foil ($23 \pm 2 \mu\text{m}$), free of antioxidant. In the membranes examined the amount of grafted polyacrylic acid varied from 20 to 80-wt%. Distilled acrylic acid (practical grade, Fluka AG) and isotactic polypropylene (M.Z.P.R., Poland) were used for membrane preparation. Before grafting, the PP foil was activated by oxygenation to form peroxide and hydroperoxide groups along the PP chains. Grafting itself was carried out at 358 K using ferrous sulfate as the activator. Degree of grafting was controlled by the time of grafting. The details of oxidizing and grafting have been presented earlier.¹³ The main properties of the membranes, i.e., the degree of grafting, water content, and the concentration of carboxylic groups are listed in Table I.

Conductivity Determinations

Membrane conductivity was measured with an ac bridge (1 kHz) by applying the method described in the literature.¹⁷ Prior to experiments, the membranes were converted to their potassium form by ion exchange in

TABLE I
The Main Properties of PP-*g*-PAA Membranes

Degree of grafting wt % of <i>g</i> -PAA in the dry membrane	Volume fraction of water, V_w	Concentration of ionic groups in the swollen mem- brane in K^+ form, C_m (mol/dm ³)
20	0.295	1.48
25	0.404	1.65
28	0.500	1.59
36	0.670	1.41
37	0.480	1.86
43	0.695	1.63
47	0.780	1.30
60	0.800	1.59
69	0.823	1.68
73	0.859	1.44

0.5M KOH solution, then they were washed with distilled water and left for equilibration in 0.1M KOH solution. To assure the precise determination of conductivity, the experiments were carried out by using a two-compartment cell with platinized-platinum electrodes mounted on two blocks at adjustable distances. The conductance was measured at 298 ± 0.1 K with the cell filled with 0.1M KOH solution alone (κ_1) and with KOH and the membrane (κ_2) by using an autobalance conductivity bridge (Meratronik E315A). The specific conductivity of the membrane was calculated from the equation

$$\kappa_m = \kappa_1 \cdot \kappa_2 \cdot l / (\kappa_1 - \kappa_2) \cdot S \quad (5)$$

where l and S denote the thickness and active area of the membrane. The results can be seen in Figure 1.

Concentration Profiles of Grafted Poly(acrylic Acid) within the Membranes

Thin slices of dyed films were photometered by using a microscope and the photometer assembly devised in our laboratory and described earlier.¹⁸ The slices were cut perpendicular to the film surface by using a microtome. A 1% solution of methylene blue in buffer solution of pH 9 was used for dyeing. Later the slices were washed with water and acetone and dried. Examples of profiles, drawn in coordinates of light absorption (A) vs. the

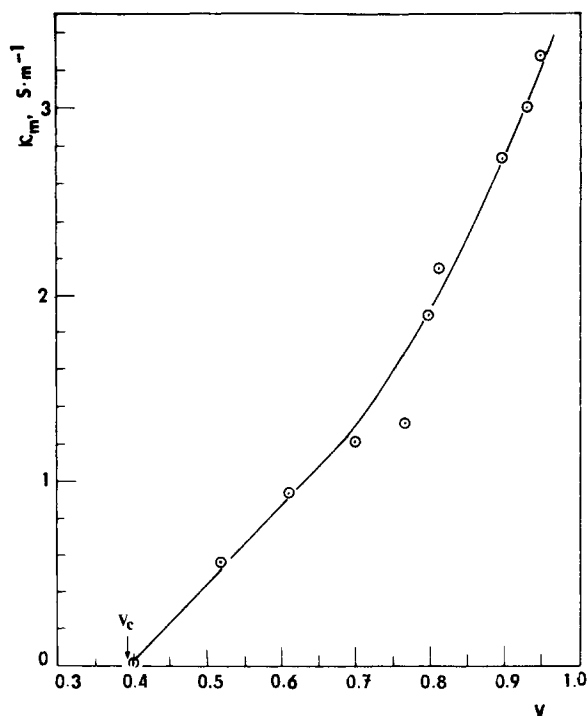


Fig. 1. Membrane conductivity dependence on the volume fraction of the conducting phase.

normalized film thickness (d/d_0), are seen in Figure 2. They demonstrate the symmetrical distribution of the ionic component within the membrane. Three "layers" are easily distinguished:

- the surface layer with almost constant fraction of grafted polyacid;
- the intermediate layer with the fraction of grafted polyacid decreasing toward the central part of the membrane;
- the central layer with the lowest fraction of the ionic polymer. In the membranes of highest degree of grafting the g -PAA gradient vanishes. When examining thin slices cut parallel to the membrane surface (XY plane), no anisotropy of the ionic component has been noted. The photometric curves were used further to calculate the volume fractions of the ionic component in each layer.

Calculation of Volume Fractions of the Ionic Component within Swollen Membranes and Layers

According to eq. (4), in order to describe the conductivity of membranes by the percolation theory the volume fraction of the internal conducting phase (V) must be known. Within the PP- g -PAA membranes this phase consisted of ion-containing polymer chains (V_{PA}), potassium counterions (V_K), and water swelling the membrane (V_w):

$$V = V_{PA} + V_K + V_w \quad (6)$$

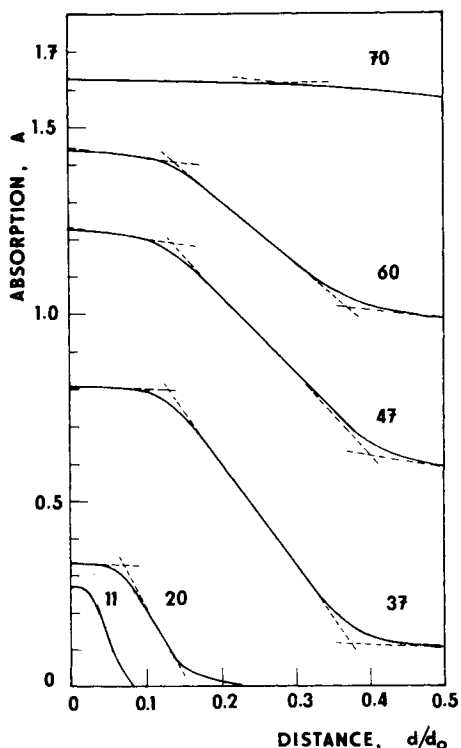


Fig. 2. Concentration profiles of g -PAA in the dry state of the grafted membranes at different graft level (wt-%).

The volume fraction of the ionic polymer was calculated after having determined the mass of grafted polyacid in the dry membrane (W):

$$V_{PA} = W \cdot (1 - V_w) / \left[W + (1 - W)d_{PA}/d_{PP} \right] \quad (7)$$

In eq. (7) d_{PA} and d_{PP} are the densities of poly(acrylic acid) and polypropylene, respectively. To calculate the volume fraction of water V_w in the swollen membrane the molar volume of water was taken to be the same as in bulk water, i.e., 18.03×10^{-3} dm³/mol. The volume fraction of potassium counterions V_K was calculated from the relation

$$V_K = C_m \cdot V_K^0 \quad (8)$$

where C_m is the molarity of carboxylic groups in the swollen membrane and V_K^0 is the partial molar volume of potassium ions at infinite dilution in water, i.e., 8.7×10^{-3} dm³/mol.

The volume fraction of conducting phase (V_i) and the relative thickness (L_i) of each of the layers in the swollen membranes have been estimated from photometric curves. In computations, proportionality between the concentration of carboxylic groups (M_i) and mean absorption (A_i) for each layer has been assumed. With this assumption one finds the relations:

$$M_1 = l_1 \cdot f(l, A) \quad (9)$$

$$M_2 = l_2 \cdot f(l, A) \cdot A_2/A_1 \quad (10)$$

$$M_3 = 0.5 \cdot C \cdot M_1 - M_2 \quad (11)$$

where

$$f(l, A) = 0.5 \cdot C \cdot (l_1 + l_2 \cdot A_2/A_1 + l_3 \cdot A_3/A_1) \quad (12)$$

In eqs. (10)–(12), C denotes the concentration of carboxylic groups (mol cm⁻³) and l_i is the thickness of the layer obtained from the photometric curve, both C and l_i referring to dry membranes.

Assuming further that, in the swollen membrane, hydration of carboxylic groups, H ($H = V_w/C_m$; for numerical values of V_w and C_m , see Table I), expressed as the volume of water per mol of $-\text{COO}^-$ groups, is constant, the volume of water in each layer $V_{w,i}$ has been calculated from

$$V_{w,i} = HM_i, \quad i = 1, 2, 3 \quad (13)$$

With the calculated values of M_i and $V_{w,i}$ from eqs. (9)–(13), it was possible to compute V_i and L_i , i.e. the thickness of the swollen layer. The results are presented in Table II.

TABLE II
The Distribution of *g*-PAA in Swollen Membranes from Photometric Data

Total volume fraction of conducting phase, <i>V</i>	Volume fraction of conducting phase in a layer			Thickness of a layer		
	<i>V</i> ₁	<i>V</i> ₂	<i>V</i> ₃	<i>L</i> ₁	<i>L</i> ₂	<i>L</i> ₃
0.40	0.83	0.59	0.03-0.08	0.08	0.11	0.31
0.52	0.84	0.63	0.10	0.10	0.15	0.24
0.61	0.86	0.68	0.15	0.12	0.18	0.20
0.70	0.85	0.70	0.33	0.15	0.24	0.12
0.77	0.89	0.77	0.37	0.14	0.24	0.12
0.80	0.89	0.79	0.58	0.15	0.26	0.09
0.86	0.92	0.86	0.74	0.14	0.27	0.09
0.90	0.92	0.90	0.87	0.15	0.23	0.12
0.93	0.93	0.93	0.93	0.25	0.23	0.02
0.95	0.95	0.95	0.95	0.25	0.25	—

RESULTS AND DISCUSSION

Critical Volume Fraction *V*_{*c*} and Critical Exponent *t* for Anisotropic Membranes

The relation of κ_m to the volume fraction of the conducting component (Fig. 1) confirms the appearance of the conductivity threshold. The CVF corresponding to the threshold point was estimated by extrapolating the curve $\kappa_m = f(V)$ to zero conductivity whereas the exponent *t* was found from eq. (4) written in the logarithmic form, i.e.,

$$\log(\kappa_m) = \text{const} + t \cdot \log(V - V_c) \quad (14)$$

Found in this way, the CVF equals 0.395 and appears to be considerably above that predicted by theory for simple heterogeneous isotropic systems (CVF \approx 0.15). Also the exponent *t*, calculated with the least-square method, has been found to be 1.21 ± 0.03 instead of 1.6 ± 0.2 , predicted by the percolation theory for three-dimensional systems. The plot of κ_m vs. (*V* - *V*_{*c*}) is presented in Figure 3. Considering that eq. (4) may be adequate for describing the system near the percolation threshold only, calculations of the exponent *t* have been repeated limiting the range of *V* - *V*_{*c*}. The results presented in Table III prove that *t* is almost constant over the whole range of volume fractions of the conducting phase. The correlation coefficient for $\log(\kappa_m)$ vs. ($\log V - V_c$) exceeds 0.99 and does not depend on the range of *V* - *V*_{*c*}, confirming that eq. (4) is appropriate for describing the conductivity of the examined membranes. Invariability of the exponent *t* over a wide range of *V* is typical of site type percolation.¹⁹ To exclude the possibility of a lowering of the exponent *t* by inaccuracy in determining *V*_{*c*}, we estimated it again by fitting eq. (4) to the experimental data and adjusting κ_0 , *V*_{*c*}, and *t* by using a nonlinear least-square non-method. With this procedure we have found $V_c = 0.382 \pm 0.002$ and $t = 1.3 \pm 0.05$. Both constants differ only slightly from those noted above. Thus one may conclude that values different from the theoretical *V*_{*c*} and *t* found here are characteristic

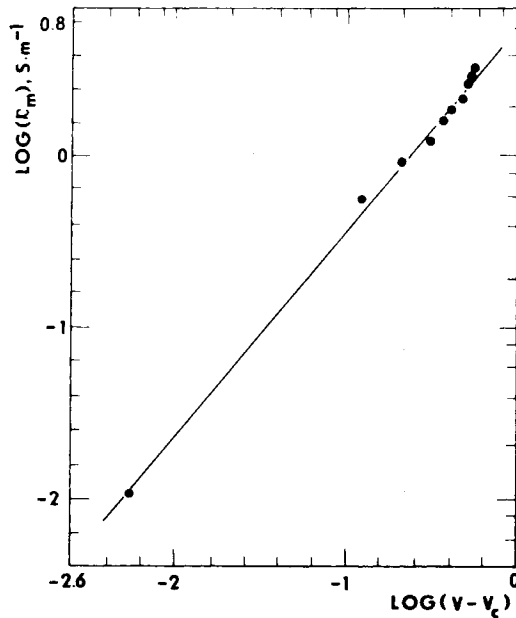


Fig. 3. $\text{Log}(\kappa_m)$ vs. $(V - V_c)$ plot for PP-*g*-PAA membranes with critical volume fraction V_c equal to 0.395.

of the membranes studied and may result from anisotropy in the membrane composition.

Critical Volume Fraction V_c and Critical Exponent t for PP-*g*-PAA Copolymer

Modeling the percolation in the membranes studied here we postulate that within each of three layers the conducting ionic polymer is distributed randomly and the layers are isotropic in composition* and, for each of

* To test how far the model with constant concentration of *g*-PAA through the intermediate layer ($i = 2$) fits the membrane structure, we allowed for a gradient in the concentration of this component; however, no significant improvement was found with this modification.

TABLE III
The Dependence of The Critical Exponent t on The Excess Volume Fraction of The Conducting Phase $(V - V_c)$

$V - V_c$ range used for calculation	Critical exponent t	Confidence limits for t , $\pm \epsilon$	Linear correlation coefficient for $\log(\kappa_m)$ vs. $\log(V - V_c)$ relationship, r
0.555	1.21	0.029	0.996
0.535	1.20	0.032	0.996
0.507	1.20	0.038	0.996
0.469	1.18	0.038	0.997
0.406	1.18	0.050	0.997
0.370	1.17	0.072	0.997
0.310	1.20	0.088	0.998
0.210	1.24	0.120	0.999

isotropic layers, eq. (4) is appropriate for describing percolation with the same V_c^* and t^* . If the specific conductivity of the grafted potassium polyacrylate is constant, independent on the layer, the resistance of a layer i can be expressed as follow:

$$R_i = L_i \cdot (V_i - V_c^*)^{-t^*} / \kappa_0 \quad (15)$$

whereas the specific conductivity of the membrane is

$$\kappa_m = 0.5 \cdot \kappa_0 \sum_{i=1}^3 L_i \cdot (V_i - V_c^*)^{-t^*} \quad (16)$$

The constants V_c^* , t^* , and κ_0 which appear in eqs. (15) and (16) differ from the previous ones (V_c , t) since they correspond to the local isotropic arrangement of PP-*g*-PAA in a particular layer. The comparison of V_c^* to V_c and t^* to t should answer to the question formulated at the beginning, i.e., how far the anisotropy of the system may influence the parameters of the percolation power law.

The values of V_c^* , t^* , and κ_0 have been computed by using the least-square nonlinear method, trying to fit eq. (16) to the experimentally determined κ_m . The best fit values and their statistical confidence limits are presented in Table IV. Bearing in mind the simplifications introduced in the model, we regard the computed V_c^* and t^* as approximate. It can be seen, however, that the critical exponent t^* corresponds to the one theoretically predicted for three-dimensional systems. According to the experimental results published by some authors,²⁰⁻²² a critical volume fraction in the range 0.7–0.10 is characteristic of polymers loaded with conducting particles.

The shape and the spatial distribution of conducting domains in heterogeneous systems can be discussed on the basis of the critical volume fraction itself and the maximum packing factor f . This factor describes the system with the conducting phase at saturation. For the membranes examined here, f is very high, exceeding 0.95. The factor f tending to unity is characteristic of bicontinuous systems. Taking into account that membranes studied were prepared by grafting acrylic acid previously introduced into polypropylene foil by diffusion, one can accept that the structure of these membranes should resemble an "alloy" with the ionic polymer appearing in the amorphous domains of polypropylene. Formed in this way, conducting

TABLE IV
Critical Volume Fraction (V_c), Critical Exponent (t), and Specific Conductivity of Ionic Component (κ_0) in PP-*g*-PAA Membranes^a

Parameter	For anisotropic membrane (from experimental data)	For isotropic local arrangement of PP- <i>g</i> -PAA (from model)
V_c, V_c^*	0.395	0.08 ± 0.05
t, t^*	1.21 ± 0.03	1.53 ± 0.32
κ_0	—	3.77 ± 0.56

^a κ_0 , S m⁻¹.

domains have possibly a fiber- or sticklike shape. The published data confirm that materials containing conducting particles of such a shape show low,²³ or sometimes very low CVF as has been found for conducting systems with fibrillar-shaped particles.¹⁵

CONCLUSIONS

The results lead to the following conclusions:

For the polypropylene-*g*-poly(acrylic acid) membranes with macroscopically anisotropic distribution of the conducting component, the conductivity threshold has been found to be at the critical volume fraction $V_c = 0.395$. This value is considerably above that predicted by theory for a system composed of randomly distributed conducting particles of regular shape. We suggest that this increase comes from a high correlation in the spatial disposition of the conducting centers within the membrane. The attainment of the CVF, enabling the formation of an infinite conducting cluster, in these membranes is limited by the concentration of the ionic component in their central part.

The CVF for the polypropylene-*g*-poly(acrylic acid) copolymer with isotropic distribution of the ionic component has been estimated as 0.08. This value is close to that characteristic of polymer composites containing non-spherical conducting particles.

The polypropylene-*g*-poly(acrylic acid) membrane with its two critical volume fractions—one local, for each layer (isotropic), and another for the whole membrane (anisotropic)—provides a system useful for verifying the invariability of the critical exponent t . The results published^{24,25} for 2-dimensional systems with anisotropy in the shapes or sizes of the conducting component suggest that t is almost constant whereas for the systems with anisotropic density of the conducting bonds t seems to depend on anisotropy. The computations presented here proved that the anisotropy in the distribution of the conducting phase causes a decrease in the exponent t in comparison with the theoretically predicted value for isotropic materials.

The power law for the percolation conductivity of the heterogeneous systems, viz.,

$$\kappa_m \sim (V - V_c)^t$$

with the constant exponent t was found to be appropriate for describing the conductivity of membranes studied over a wide range of volume fraction of the conducting component, i.e., from percolation threshold up to $V = 0.9$.

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