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DIFFUSION INTO POLYPROPYLENE OF CHLORIDES OF ALKALI METALS

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Abstract—Diffusion of lithium, sodium and potassium chlorides from aqueous solutions into polypropylene (PP) was studied. The changes in polarity of the PP surface were examined by measurement of contact angles and the depth distribution of the diffusing atoms was determined using Rutherford backscattering (RBS) and neutron depth-profiling (NDP). The sorption of the chlorides results in increase in the surface polarity. Irregular diffusion of LiCl into PP was observed.

INTRODUCTION

Recently several methods have been suggested for the modification of polymer surface properties and structure. Irradiation of the polymer with excimer laser [1], proton beam [2] and ion beam [3] can be employed. By these techniques, only very thin ($< 1\ \mu m$) surface layers are modified. Another, more conventional method for introducing inorganic agents into polymers and modifying their properties is diffusion of inorganic salts from aqueous solutions.

Inorganic salts in the solid state cannot diffuse into polypropylene (PP) or polyethylene(PE) [4]. No penetration of sodium ions through PE film has been observed [4]. From aqueous solutions of inorganic salts, only water diffuses into PE but its diffusion rate decreases with increasing salt concentration, i.e. with decreasing water activity [4]. Most inorganic salts and their aqueous solutions do not diffuse into PP and do not affect its mechanical properties at temperatures below 100°C [4]. On the other hand, ion diffusion from aqueous $FeCl_3$ into polyacetylene films has been observed [5].

In this work, the diffusion of lithium, sodium and potassium chlorides from aqueous solutions into PP was investigated with the aim of determining the diffusion rate and the resulting depth distribution of the diffused salt in the polymer. The resulting changes of the polarity of the PP surface are also examined.

EXPERIMENTAL PROCEDURES

The experiments were performed on $15\ \mu m$ thick films of oriented PP with $\bar{M}_n$ of 150,000 and density of $0.901\ g \cdot cm^{-3}$. The diffusion of LiCl, NaCl and KCl salts was performed from aqueous solutions at their boiling points (103–105°C). Solutions with concentrations 3.0 and $5.0\ mol \cdot l^{-1}$ were used; for LiCl, a solution of $10.0\ mol \cdot l^{-1}$ could also be employed because of its higher solubility.

After the samples had been exposed to the solutions, the polar component of the free surface energy γ_s^p was determined by measuring the contact angle using a technique suggested earlier [3]. The total amount and the concentration depth profile of diffused atoms were measured using the usual Rutherford backscattering (RBS) technique with 1.3 MeV α-particle beam from an electrostatic Van de Graaff accelerator. The laboratory scattering angle was 160° and the beam intensity was kept below 5 nA in order to avoid thermal degradation of the sample. The α-particles scattered from the sample were recorded by a Si(Au) surface barrier detector, the system energy resolution being full with a half maximum (FWHM) of 15 keV.

The Li atom content was also determined using the neutron depth-profiling method (NDP) which is based on the $^6Li(n,\alpha)^3H$ nuclear reaction induced by thermal neutrons. The PP samples were irradiated with a thermal neutron beam from a 6 m neutron guide (neutron flux $4.5 \times 10^6\ sec^{-1} \cdot cm^{-2}$) and charged reaction products were recorded by means of a Si(Au) surface barrier detector. The principles of the NDP technique and details of the experimental arrangement have been given [7].

RESULTS AND DISCUSSION

The dependence of the surface free energy γ_s^p on the time for which the PP was exposed to the solution is shown in Fig. 1. The pristine PP has $\gamma_s^p = 2.5\ mJ \cdot cm^{-2}$ while the dispersal component of the free surface energy is $\gamma_s^d = 31.8\ mJ \cdot cm^{-2}$. The latter value is close to the value $\gamma_s^p = 30.2\ mJ \cdot cm^{-2}$ reported [6] but the type of PP was not specified. It is evident from Fig. 1 that diffusion from 3 M solutions of LiCl and NaCl results in about a twofold increase of γ_s^p after 15 min exposure and no further increase is observed for longer exposures. On the other hand, in 3 M solution of KCl, the polar component of the surface free energy increases steadily with increasing exposure.

For 5 M solutions, the process proceeds differently. For the LiCl solution, the polar component γ_s^p increases rapidly and, after 120 min exposure, its value is about 10 times the original. In NaCl and KCl solutions, significant increase of the polar component takes place only after 60 min exposure. One can also see from comparison of Figs 1(a)–(c) that, for $5\ mol \cdot l^{-1}$ solutions and for all exposure times, the polar component decreases with increasing atomic

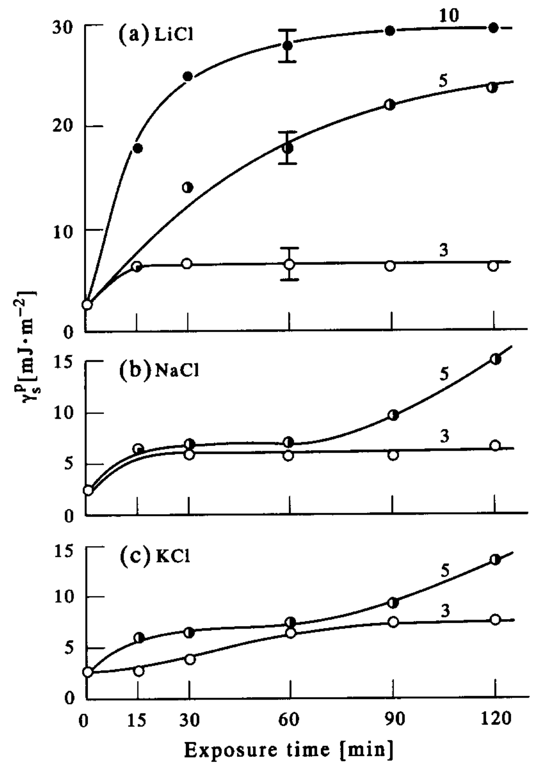

Fig. 1. The dependence of the polar component of the surface free energy (γ_s^p) of PP on the exposure time in aqueous solutions of chlorides of alkali metals. The numbers give the solution concentration in mol·l^{-1}.

number of the cation. The latter finding is in accord with the well known fact that the diffusion depends on the size of diffusing particles. The diffusion evidently depends also on the particle concentration in the source. This fact is confirmed by the present observation of the increase of γ_s^p when the chloride concentration is raised from 3 to 5 M or to 10 M in the case of LiCl. From the measured dependence of γ_s^p on the exposure time for LiCl (Fig. 1), one can see that the diffused particle content in PP achieves a saturation value. The exposed PP samples were examined after three months but no further changes of the surface polarity were observed.

The PP samples exposed to 5 and 10 M chloride solutions were analysed using the RBS method in order to determine the content and the depth distribution of the diffused particles. The energy spectrum of 1.3 MeV α-particles scattered from the PP sample exposed for 60 min in 5 M solution of LiCl is shown in Fig. 2. Besides the distribution below 500 keV, due to α-particle scattering from bulk carbon atoms, one can see a weak signal just below 900 keV corresponding to α-particles scattered from Cl atoms embedded in the surface layer of PP. Very small surface contamination with oxygen ($< 3 \times 10^{15}$ cm^{-2}) is also observed; it may be due to water diffusion. The presence of Cl atoms was observed only in PP samples exposed to the solutions of NaCl and KCl, the concentrations of both chlorine and the metals were below the RBS detection limit of about 1×10^{15} cm^{-2}. Despite very long measuring times, the RBS measuring statistics remain low and the calculated area densities of Cl atoms are subject to large statistical uncertainties. Moreover the RBS technique is not sensitive to Li atoms because of their low mass. More representative data were therefore obtained using the NDP technique sensitive to ^{6}Li isotope, the real detection limit being as low as 10^{13} cm^{-2}. The energy spectrum of the reaction products from ^{6}Li(n,α)^{3}H, measured on the same sample as in Fig. 1, is shown in Fig. 3. The Li atom area densities as a function of the exposure time and the solution concentration obtained from NDP analyses are

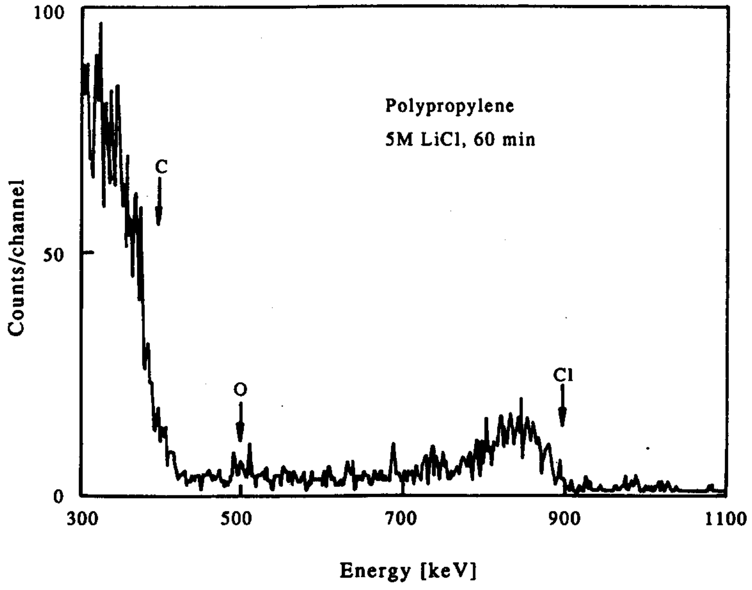

Fig. 2. The energy spectrum of 1.3 Mev α-particles scattered under 160° laboratory scattering angle from PP samples treated in 5 M solution of LiCl for 60 min.

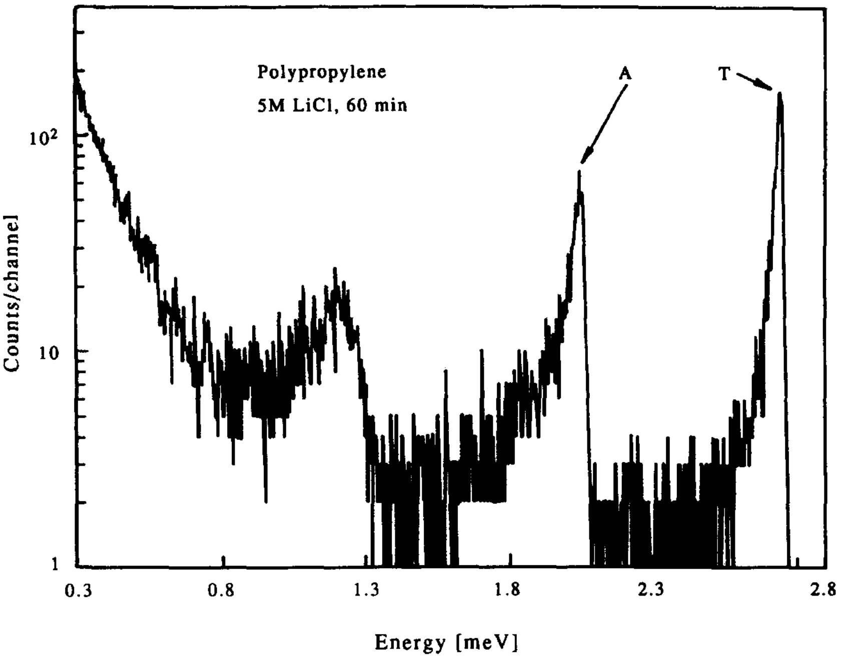

Fig. 3. The energy spectrum of charged particles emitted in the $^6Li(n,\alpha)^3H$ reaction. The measurement was performed on the sample referred in Fig. 2. The peaks denoted by A and T belong to alpha particles and tritons respectively. The Li depth profile was deduced from peak A transforming the particle energy into depth and count number into the concentration of Li atoms.

summarized in Table 1. The corresponding densities of Cl atoms obtained from RBS measurements are within experimental uncertainties equal to those of Li atoms, in accord with LiCl stoichiometry.

From Table 1, one can see that the LiCl content increases rapidly with increasing exposure and reaches a maximum for 60 min exposure. The maximum contents are proportional to the concentration of the chloride solution. For 90 and 120 min exposures, a significant decrease of the LiCl content is observed in both RBS and NDP measurements. The initial fast increase in the LiCl content satisfies an approximate relation $c \sim t^{(1.5 \pm 0.5)}$ (where c is the LiCl content and t is the exposure time). So that, the increase of the LiCl content is much faster than for regular Fickian diffusion for which $c \sim t^{0.5}$ is expected.

The irregular LiCl behaviour is also seen from Fig. 4 in which the Li atom depth profiles obtained from NDP measurements are shown for the PP samples exposed to 5 and 10 M aqueous solutions of LiCl for 60 min. The Li atom depth profiles were obtained for all PP samples examined and they exhibit the same shape as those in Fig. 4, i.e. the profiles are characterized by a sharp surface maximum and exponential decrease of concentration towards the interier of the sample. Therefore the depth profiles do not follow error function (Erfc)

Table 1. The dependence of Li atom area density in the PP samples exposed to an aqueous solution of LiCl on the solution concentration and the exposure time. The Li contents were obtained by the NDP technique. Each quoted value is the mean of two independent measurements

Exposure time (min)	Solution concentration (10^{15} cm^{-2})*	
	5 M	10 m
15	3.7	7.6
30	16.2	18.5
60	17.5	35.6
90	13.4	26.6
120	12.1	16.0

*The Li area densities are stated with 5% statistical uncertainty.

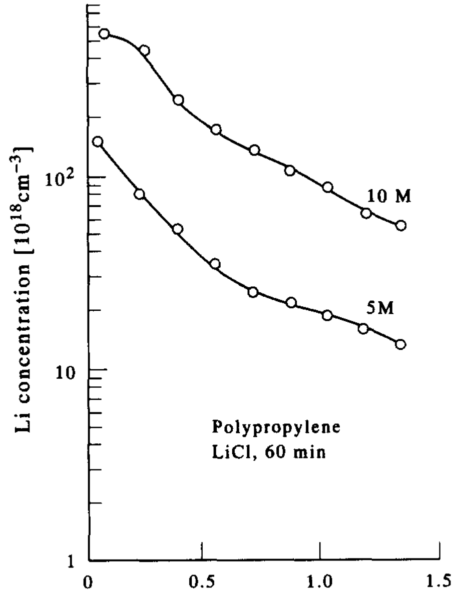

Fig. 4. The concentration profiles of Li atoms determined from NDP measurements for the PP samples exposed for 60 min to 5 and 10 M solutions of LiCl.

dependence expected for regular LiCl diffusion from an infinite source. Experimental points of the depth profiles were determined with 5% relative statistical error.

These experimental findings, together with the observed decrease of LiCl content for longer exposure times, lead to the conclusion that the incorporation of LiCl in PP is a rather complicated process. The saturation and subsequent decrease in LiCl content may be due to some molecular or ion exchange at PP/solution interface but the detailed mechanism of these phenomena remains unknown.

CONCLUSION

It was shown that, during the exposure of PP to aqueous solutions of LiCl, NaCl and KCl, diffusion of inorganic salts into the polymer occurs and the polarity of the polymer surface increases. The diffusion rate depends on the size and on the initial concentration of the diffusing species. The dependence of the Li content on exposure time and the Li depth profiles were measured using RBS and NDP techniques. The LiCl diffusion is faster than expected from Fick's law, the Li content being proportional to exposure time to the (1.5 ± 0.5) power. This time dependence indicates rather rapid diffusion. The Li atom depth profiles exhibit a pronounced surface maximum and an exponential decrease towards the interior of the sample. The diffusion coeficient was estimated to be as low as $10^{-14}\,\mathrm{cm}^2\cdot\mathrm{sec}^{-1}$. Only very small traces of surface oxygen were observed, so that the autooxidation of PP and/or the diffusion of water or oxygen into PP are very slow.

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