Electrokinetic Properties of Acrylic Acid- and Methacrylic Acid-Grafted Polypropylene during Chemically Initiated Graft Copolymerization

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Synopsis

Electrokinetic properties such as zeta potential (ζ), surface charge density (σ) and surface conductivity (K_s) of polypropylene fibers and those grafted with acrylic acid and methacrylic acid have been studied using the streaming potential method. At pH 7, the zeta potential of -58.5 mV for control fibers reduced with increase in the amount of acrylic acid (16.2%) and methacrylic acid (28.2%) grafts to -38.15 mV and -38.30 mV, respectively. The drop in the negative zeta potential value is attributed to rendering polypropylene hydrophilic. The acrylic acid graft was found to be more effective than the equivalent amount of methacrylic acid graft in this respect due to the different chemical characters of the two graft copolymers. The negative zeta potential was also reduced to a considerable extent when cationic dye solution was streamed through the grafted polypropylene fibers, which is attributed to the deposition of dye cations on the negatively charged surface of the grafted fibers. The results on surface charge density and surface conductivity also indicated the hydrophilic character of grafted polypropylene.

INTRODUCTION

In recent years, considerable interest has been shown by research workers in the study of various aspects of polypropylene fibers, possibly due to its many potential end uses in the field of textiles and other industrial applications. Polypropylene, being an inert synthetic polymeric fiber, devoid of any functional polar groups in the fiber structure, cannot be dyed with organic dyestuffs. This is especially true with aqueous dye solutions. Moreover, it has no affinity for many commonly used industrial organic chemicals. Polypropylene develops very high static electricity in the dry state and also acquires considerable amount of a negative charge when exposed to aqueous solutions. These processes can be very well understood by the study of electrokinetic properties of the polypropylene fibers before and after their chemical modifications.

Suzawa and Yuzawa[1] studied zeta potential and surface charge density of polypropylene and other synthetic fibers in presence of surface active agents and observed that the amount of surface active agent adsorbed per unit area of the fiber surface was the highest in case of polypropylene fibers as compared to the other synthetic fibers because of its very high hydrophobicity. Fumoto, Katayama, and Kuroki[2] studied the zeta potential of

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halogenated polypropylene fibers at different pH values and also in cationic dye solutions and observed that the fluorinated polypropylene fibers had the highest zeta potential.

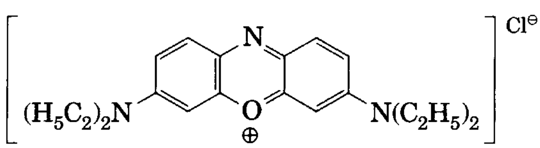
In our laboratories, research is being conducted to incorporate various functional polar groups into the structure of polypropylene fibers through graft copolymerization reactions using both chemical initiation and γ-ray irradiation techniques. In addition, we are studying various aspects, such as the kinetics of graft-copolymerization reactions with vinyl monomers,[3] as well as the electrokinetic properties of these polymers. The present paper reports the results on zeta potential, surface charge density, and surface conductivity of polypropylene fibers grafted with acrylic acid and methacrylic acid using a chemical initiation technique for graft copolymerization.

EXPERIMENTAL

Materials

Polypropylene Fibers. "Proplan" polypropylene fibers, obtained from M/s. Neomer Ltd., India, were used in the present investigation. The fibers were highly isotactic.

Dye. A cationic dye, Sandocryl Blue B3G (C.I. Basic Blue 3) was used in the present studies, having the following structure:



Purification of Dye

Purification of the cationic dye was carried out according to the method suggested by Balmforth et al.[4] The dye was extracted with 10 volumes of boiling absolute alcohol. Easily filterable crystals were recovered after chilling the solution overnight. This procedure was repeated thrice to ensure good purity of about 99.9%.

Grafting of Polypropylene Fibers

The polypropylene fibers were grafted with acrylic acid and methacrylic acid monomers by chemical initiation technique using benzoyl peroxide as an initiator. The method of grafting has been described in our earlier communications[5]. In general, the grafting efficiency was lower for AA monomer (3% maximum efficiency), but it was very high in case of MA monomer (55% maximum efficiency).

Determination of Electrokinetic Properties

Determination of streaming potential, calculation of zeta potential, surface charge density, and surface conductivity have been discussed in a previous communication[6]. The pH of the dye solution was at 7. Reproducibility of the measurements was fairly good, (±1.0 mV).

RESULTS AND DISCUSSION

Polypropylene as well as fluorinated polypropylene was shown to have large amount of negative zeta potential due to very high hydrophobicity of these fibers.[1,2] In the present investigation, hydrophilicity is imparted to polypropylene through graft copolymerization of acrylic acid (AA) and methacrylic acid (MA) monomers. The electrokinetic properties of the grafted fibers, such as zeta potential, surface charge density, and surface conductivity, have been studied.

Figure 1 gives the relation between negative zeta potential and graft add-on at pH 7. The results indicate that the negative value of zeta potential decreases with increase in the AA and MA graft contents in polypropylene. Thus, zeta potential of −58.50 mV for the control is reduced to −38.15 mV and −38.30 mV, when the AA and MA grafts of 16.2% and 28.2%, respectively, were introduced in the polypropylene fibers. The results suggest that due to introduction of grafts in polypropylene, the polymer is rendered more and more hydrophilic, and, hence, there is a drop in the negative

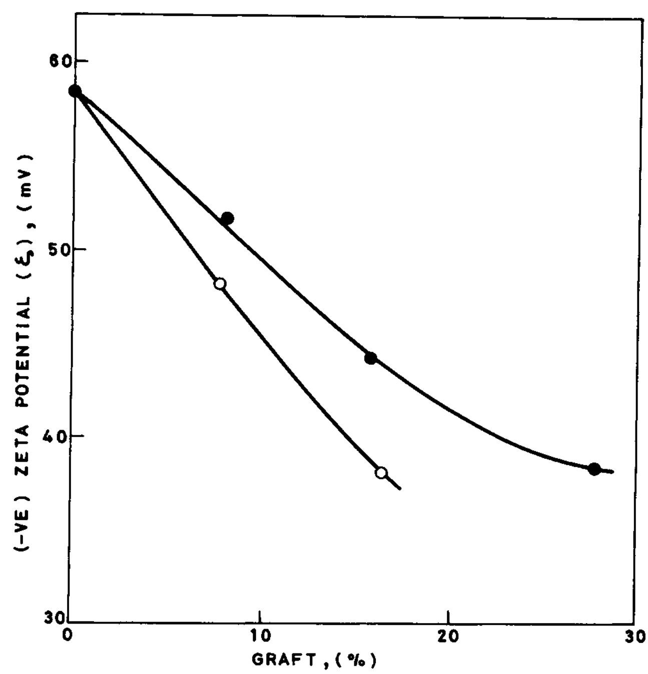


Fig. 1. Relation between zeta potential and graft % onto polypropylene fibers: (○) AA graft; (●) MA graft.

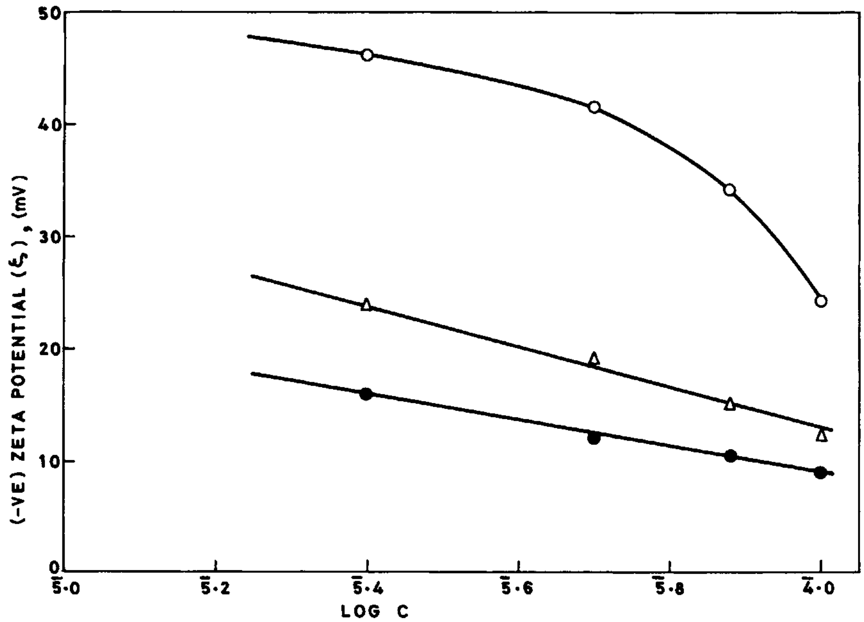


Fig. 2. Relation between zeta potential and log (dye concentration): (○) 0% AA; (△) 7.6% AA; (●) 16.2% AA.

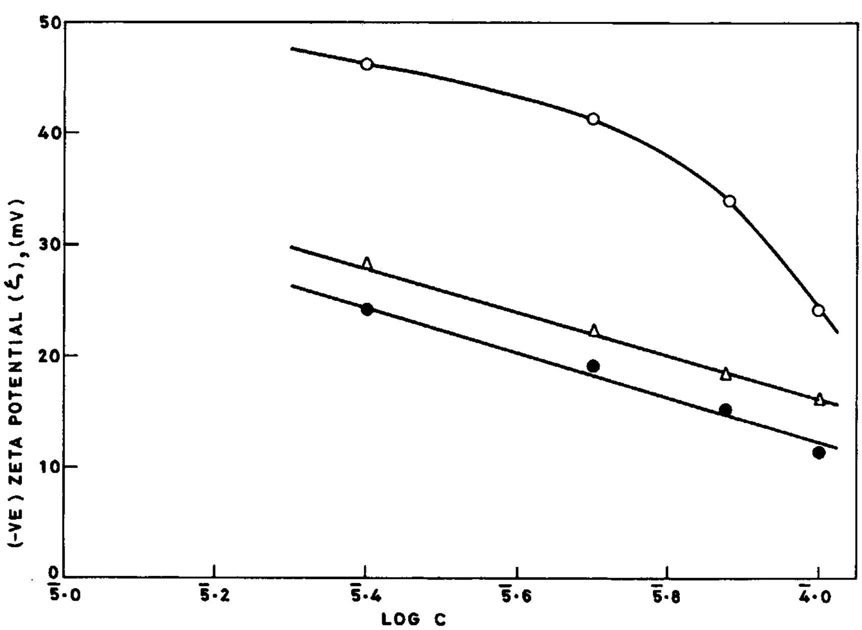


Fig. 3. Relation between zeta potential and log (dye concentration): (○) 0% MA; (△) 8.1% MA; (●) 15.6% MA.

value of zeta potential. The drop in negative zeta potential is greater in case of AA graft as compared to the equivalent amount of MA graft in the fiber. This may be attributed to the fact that AA graft imparts greater hydrophilicity to the fiber as compared to the MA graft.

With a view of investigating the effect of streaming cationic dye solution on the electrokinetic properties of grafted polypropylene, solutions of varying concentrations of a cationic dye—Sandocryl Blue B3G (C. I. Basic Blue 3)—were streamed through the AA-grafted and MA-grafted polypropylene fibers. The results with respect to zeta potential are shown in Figures 2 and 3. In general, the results indicate that the negative zeta potential decreases with an increase in the concentration of dye solution for control as well as grafted polypropylene fibers. This may be attributed to the deposition of the cationic dye molecules on the negatively charged fibers (as may be the case for control) as well as adsorption of the dye cations at the carboxylic groups of the grafts. The drop in negative zeta potential is greater for higher levels of AA and MA grafts as a result of greater and greater number of—COOH groups present in the fibers being available for interaction with the dye cations in the streaming solution. The absolute values of the drop in negative zeta potential in case of MA graft are lower as compared to those observed in case of AA graft in fiber, because the MA graft may contain a smaller number of—COOH groups as compared to the equivalent amount of AA graft, due to its higher molecular weight. For a given equivalent mol % graft of AA and MA, the decrease in the zeta potential in case of MA-grafted polypropylene may also be lower due to the

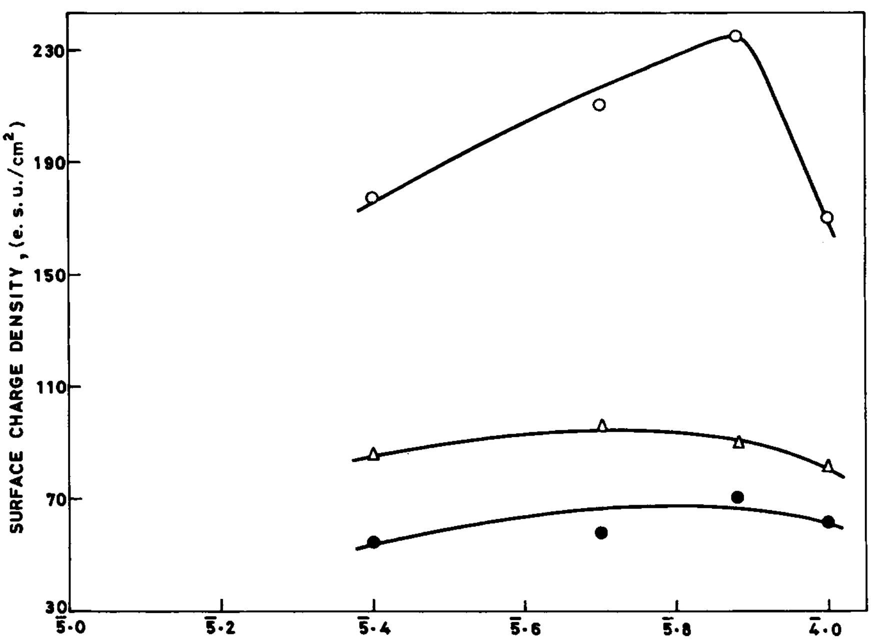


Fig. 4. Relation between surface charge density and log (dye concentration): (○) 0% AA; (△) 7.6% AA; (●) 16.2% AA.

lower degree of ionization of MA due to substitution of—CH_3 in place of —H in AA.

Figures 4 and 5 give the plots of surface charge density against log of dye concentration in the streaming solution. The surface charge density of the control increases with increase in the dye concentration up to about $7.5 \times 10^{-5} M$ of the dye in solution, but drops beyond this point. The increase in the surface charge density seems to be due to increase in the number of ions in the vicinity of the fibers, and the subsequent decrease at very high concentrations of the dye may be due to the reduction in the thickness of the electrical double layer containing a larger number of dye cations. The curves for the grafted polypropylene fibers have more or less similar trend for the control, except that there is no sharp break and also the absolute values of surface charge density are lower at higher amounts of grafts in the polymer. This may be due to the change in the nature of the fiber characteristics from hydrophobic to hydrophilic as a result of AA and MA grafts introduced in polypropylene.

Results on surface conductivity are given in Figures 6 and 7, with respect to AA and MA grafts, respectively. It can be seen that the surface conductivity is minimum at $7.5 \times 10^{-5} M$ concentration of the cationic dye in the streaming solution. The minima shift to a lower level of $5 \times 10^{-5} M$ of dye concentration for the AA- and MA-grafted polypropylene fibers. These results may be attributed to the saturation of the surface of grafted polypropylene, which occurs at a much lower concentration of the dye in solution

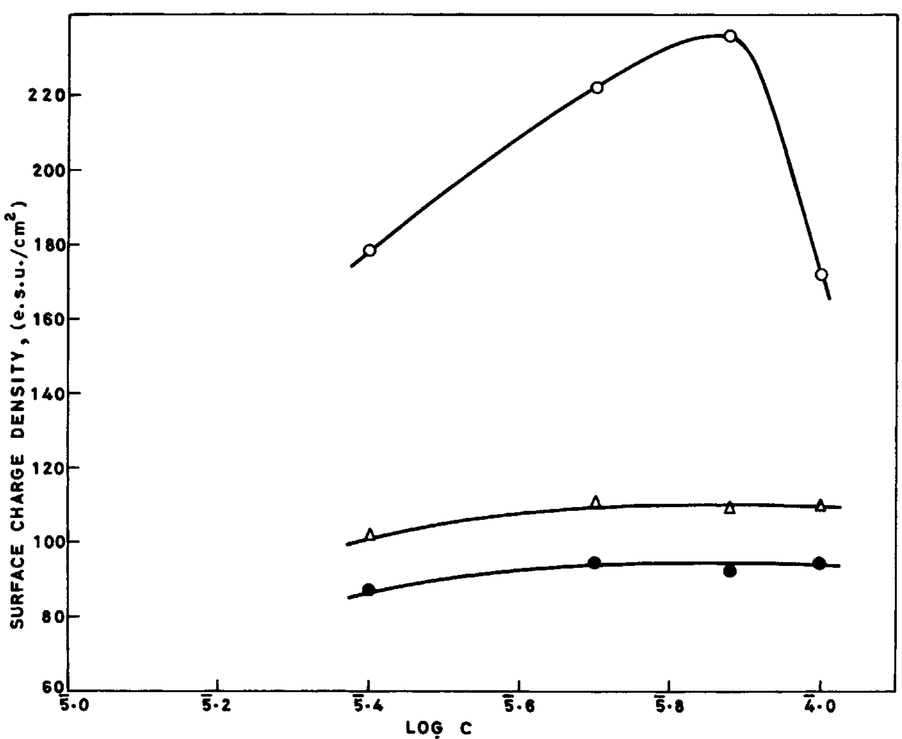


Fig. 5. Relation between surface charge density and log (dye concentration): (○) 0% MA; (△) 8.1% MA; (●) 15.6% MA.

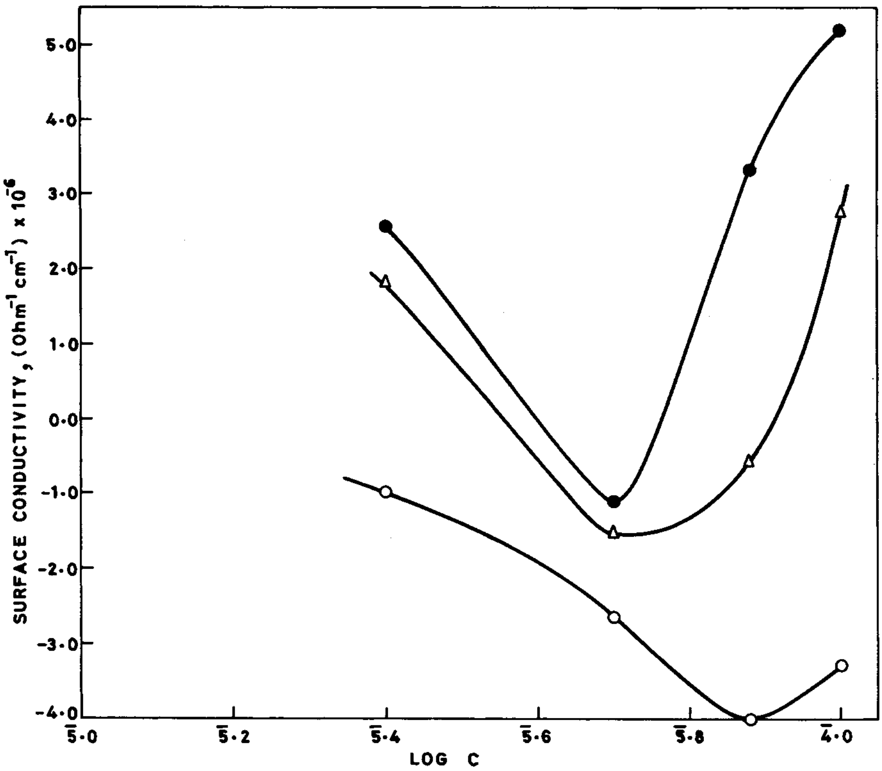


Fig. 6. Relation between surface conductivity and log (dye concentration): (○) 0% AA; (△) 7.6% AA; (●) 16.2% AA.

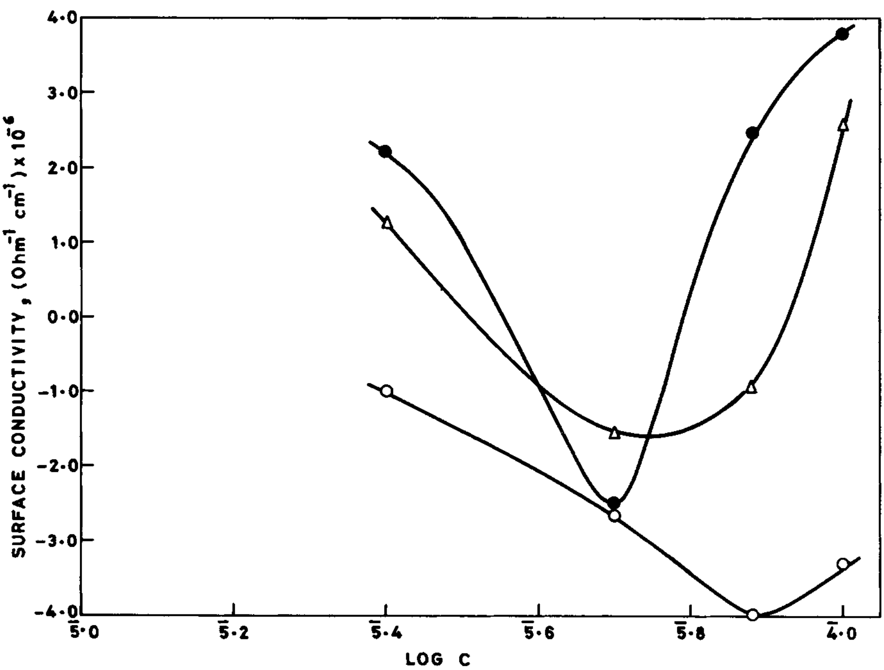


Fig. 7. Relation between surface conductivity and log (dye concentration): (○) 0% MA; (△) 8.1% MA; (●) 15.6% MA.

as a result of absorption of dye cations at the functional groups in the grafted polymer.

The results, in general, suggest that considerable amount of hydrophilicity can be induced in polypropylene through introduction of polar functional groups, such as—COOH, through graft copolymerization reactions of AA and/or MA, as evidenced from electrokinetic studies of the polymer. It is also noticed that the adsorption characteristics as well as the absorption capacity of ions, such as cationic dye molecules, are increased to a considerable extent as a result of chemical modification brought about by the grafting reactions. The grafting reactions also effect changes in the surface characteristics of the polymer as can be seen from surface conductivity studies. The fibers were not degraded to any considerable extent at the levels of 16.2% and 28.2% AA and MA grafts, respectively, although, at very high levels, say about 100%, the fibers were excessively damaged and the graft copolymers were obtained in powder form.

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