

Improving Antistatic Properties of Poly(methylvinylpyridine)–Poly(ethylene Terephthalate) Graft Copolymers Via Alkylation

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Synopsis

The alkylation reaction of poly(methylvinylpyridine)–poly(ethylene terephthalate) graft copolymers with different alkylating agents using monochloroacetic acid has proved to be the best as far as degree of alkylation and enhancement in electrical conductivity caused thereby are concerned. Kinetic investigation revealed that alkylation follows a second-order reaction, and the apparent activation energy is 15.23 cal/mole.

INTRODUCTION

Poly(ethylene terephthalate) fibers (PET) are known to be subject of static buildup. The accumulation of static charges results in the garment clinging to the body, which may be objectionable. The magnitude of electrostatic charge of fiber is represented by the balance between the rate of formation of the charge and the rate of its dissipation. Control of the latter appears to be more practical, mainly because we lack knowledge of the correlation between fiber structure and generation of the charges. Hebeish et al.¹ have disclosed that electrostatic charge on PET fiber can be reduced through vinyl graft polymerization.

The present work describes alkylation of PET grafted with 2-methyl-5-vinylpyridine (MVP) using different alkylating agents. Furthermore, the ability of poly(MVP)–PET graft copolymers before and after alkylation to control static buildup is investigated.

EXPERIMENTAL

Poly(MVP)–PET graft copolymers were synthesized by a method described by Shalaby et al.² using Trevira, Hoechst-1,2 den/4 mm, cotton type, freshly distilled MVP, and benzoyl peroxide.

Alkylation was carried out in a 50-ml stoppered flask. An accurate weight of the copolymer was introduced into 50 ml aqueous solution at a specific temperature. To this, the calculated amount of the alkylating agent was added. The flask was then immediately stoppered and placed in a thermostatted water bath. After the desired reaction time the contents were filtered on a sintered glass crucible, washed with water, dried in an oven at 50°C for 5 hr, cooled to room temperature, and weighed. The degree of alkylation was calculated as follows:

$$\% \text{ degree of alkylation} = \frac{A}{B} \times 100$$

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TABLE I
Effect of Nature of Alkylating Agent on Degree of Alkylation of Pyridine Moieties of the Graft and Electrical Conductivity of the Polymer^a

Alkylating agent	Degree of alkylation, %	$\gamma \times 10^{13}$, $\text{Ohm}^{-1} \text{mm}^{-1}$
ClCH_2COOH	9.41	1470.00
Cl_2CHCOOH	4.84	255.50
Cl_3CCOOH	1.80	18.50
	3.03	30.37

^a Graft yield 14%, temperature 90°C.

where A is the increase in weight of the copolymer due to alkylation and B is the initial weight of the graft copolymer.

The electrical resistivity was measured on an electrometer (type Van-II, East Germany).

RESULTS AND DISCUSSION

To start with, poly(MVP)-PET graft copolymers having a graft yield of 14% were reacted independently under similar conditions with monochloroacetic acid, dichloroacetic acid, and epichlorohydrin. The results obtained are shown in Table I. It is clear that the degree of alkylation depends upon the reactivity of alkylating agent with respect to the pyridine moieties of the graft. Current data suggest the following order:

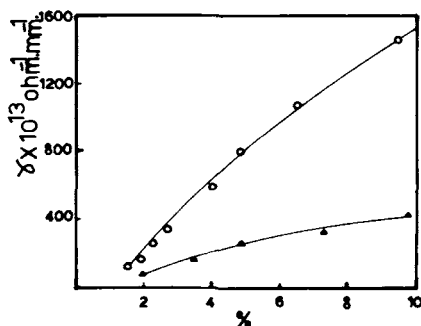


Fig. 1. Effect of degree of alkylation of the graft copolymer on electrical conductivity: (O) monochloroacetic acid; (▲) dichloroacetic acid.

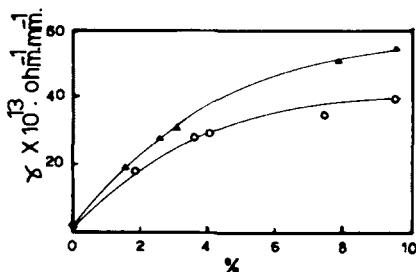


Fig. 2. Effect of degree of alkylation of the graft copolymer on electrical conductivity: (▲) epichlorohydrin; (O) trichloroacetic acid.

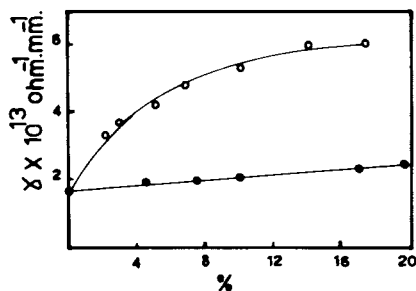


Fig. 3. Effect of graft yield on the electrical conductivity of PET: (○) PPA; (●) PMVP.

monochloroacetic acid > dichloroacetic acid
> epichlorohydrin > trichloroacetic acid

Figure 1 shows the dependence of electrical conductivity on the degree of alkylation of the pyridine moieties of the graft when monochloroacetic acid and dichloroacetic acid were used as alkylating agents. It is clear that increasing the degree of alkylation is accompanied by a significant enhancement in the magnitude of electrical conductivity. This is observed regardless of the alkylating agent employed within the range examined. However, at the same degree of alkylation, the nature of the alkylating agent plays a key role in the magnitude of the electrical conductivity. The electrical conductivity obtained with copolymers alkylated with monochloroacetic acid is strikingly higher than that obtained with their mates alkylated with the other alkylating agents.

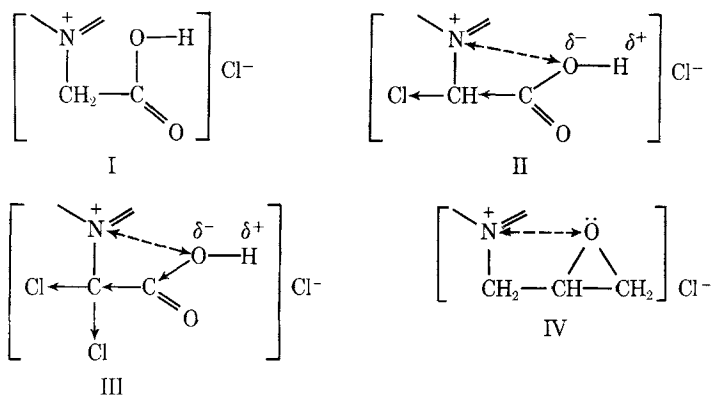
The foregoing could be explained in terms of the mode of interaction of the alkylating agent with the pyridine moieties of the graft, which may be represented

TABLE II
Kinetic Data of the Alkylation Reaction with Monochloroacetic Acid at 90°C^a

$A_0 \times 10^4$, moles	$B_0 \times 10^4$, moles	Duration, min	X	K , l./mole-min
2.17	9.71	30	0.10	73.00
2.14	9.70	60	0.17	65.40
2.11	9.71	120	0.31	66.20
1.92	9.80	360	0.53	68.40
1.90	9.74	360	0.67	68.60
4.23	9.52	60	0.18	72.20
4.06	9.80	120	0.31	68.00
3.97	9.67	240	0.51	69.80
4.11	9.70	360	0.68	79.40
7.99	9.65	60	0.18	74.20
7.83	9.78	75	0.21	70.60
8.17	9.63	120	0.32	78.60
8.27	9.75	180	0.41	75.20

^a A_0 = PMVP; B_0 = ClCH_2COOH ; K = rate constant; X = conversion.

as follows:



It will be observed that attachment of monochloroacetic acid to the pyridine moiety accentuates and/or generates complete charge on the N of the pyridine since there is no inductive effect of chlorine in this case. It is understandable that the inductive effect of chlorine favors dissociation of the carboxylic groups of the acid. This is indeed the case with respect to dichloroacetic acid and trichloroacetic acid. Enhancement of the carboxylic group dissociation promotes the interaction between the negatively charged carboxylic groups and the positively charged N in the pyridine. As a result, the polarity decreases. Similarly, decreased polarity would be expected with copolymers alkylated with epichlorohydrin due to involvement of the oxygen of the latter in an interaction with the N of pyridine. Thus, it is clear that although all alkylated copolymers contain a nitrogen atom to which is attached one ionizable chlorine, yet the effectiveness of the latter in increasing electrical conductivity is dependent of the nature of the alkylating agent (Fig. 2).

It may be argued that the presence of carboxylic groups in case of the chlorine derivatives of acetic acid are responsible for the enhancement in electrical conductivity. However, the carboxylic groups seem to contribute little in this regard,

TABLE III
Effect of Temperature on the Rate of Alkylation of Pyridine Moieties of the Graft Copolymers with Monochloroacetic Acid

Temperature °C	$A_0 \times 10^4$, moles	$B_0 \times 10^4$, moles	X_c	K , l./mole-min	Mean K , l./mole-min	
50	5.11	8.27	120	0.025	5.14	5.12
	4.75	7.99	180	0.035	5.02	
	4.57	8.22	240	0.049	5.16	
	5.06	8.24	360	0.072	5.14	
70	5.11	8.06	60	0.050	21.60	20.8
	5.38	8.20	120	0.080	21.00	
	5.06	8.69	240	0.180	20.20	
	4.97	8.50	360	0.250	20.40	
90	6.26	9.59	45	0.150	79.40	74.1
	6.21	9.65	60	0.190	78.00	
	6.29	9.73	120	0.300	68.20	
	6.02	9.70	180	0.410	70.80	

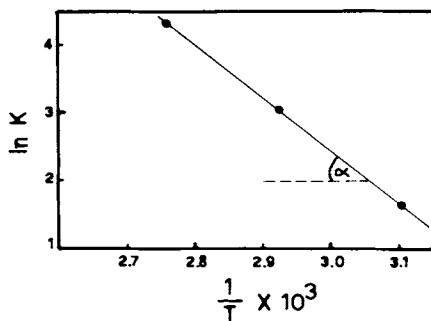


Fig. 4. Arrhenius plots for graft copolymer alkylated with monochloroacetic acid.

as can be seen from Figure 3. The latter shows that creation of a good amount of carboxylic groups in the PET molecules through grafting with acrylic acid enhances the electrical conductivity of PET to an extent that is substantially higher than PET grafted with MVP. But this enhancement in electrical conductivity is much lower than that obtained with poly(MVP)-PET graft copolymers alkylated with the chlorine derivatives of acetic acid, indicating that it is the ionizable chlorine in the alkylated copolymer which is responsible for the improved electrical conductivity of PET.

KINETIC STUDIES OF ALKYLATION REACTION

It has been shown above that monochloroacetic acid was proved to be the best alkylating agent for poly(MVP)-PET graft copolymers as far as the degree of alkylation and magnitude of electrical conductivity caused thereby are concerned. For these reasons, it is of interest to study the kinetics of this alkylation reaction.

Kinetic data of alkylation reaction occurring between poly(MVP)-PET graft copolymers and monochloroacetic acid are shown in Table II. The data indicate that the reaction follows a second-order reaction which can be represented by the following:

$$\ln \frac{M - X_A}{M(1 - X_A)} = C_{A_0}(M - 1)Kt$$

where $M = C_{B_0}/C_{A_0}$; X_A is the conversion; $C_{A_0} = \text{PMVP}$; C_{B_0} is the $[\text{ClCH}_2\text{COOH}]$; and $K = \text{rate constant}$. Based on the data of Table II,

$$r = 72.12C_A C_B$$

where r is the rate of alkylation at 90°C .

In order to obtain the apparent activation energy, the rate of alkylation reaction was studied at three temperatures, namely, 50, 70, and 90°C . The results obtained are shown in Table III.

The apparent activation energy for the alkylation reaction was calculated from an Arrhenius plot of the rate constant at different temperature versus $1/T$ (Figure 4); it amounts to 15.23 kcal/mole.

References

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2. S. E. Shalaby, A. M. Bayazeed, and A. Hebeish, *J. Appl. Polym. Sci.*, **22**, 1359 (1978).

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