

고분자 물질들의 분극 특성: Poly(vinylchloride), Poly(ethyleneterephthalate), Poly(propylene), Poly(carbonate)

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Polarization Characteristics of Polymers: Poly(vinylchloride), Poly(ethyleneterephthalate), Poly(propylene), and Poly(carbonate)

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요약: 우리는 고분자 물질들에 대해서 전위와 전류 밀도의 변화를 측정하였다. 온도와 pH를 포함하여 전위와 속도에 대한 영향을 주는 여러 요인들에 밝히기 위하여, 연구 결과들이 주위 깊게 조사되었다. 양극 해리에 대한 Tafel 기울기는 이들 조건 하에서 분극 효과로 결정되었다. 각 경우에 최적 조건들이 확립되었다. 두 번째 양극 전류 밀도 피크와 최대 전류 밀도는 상대적 분극 감도(I_p/I_c)로 지정되었다. 최적 조건에서의 분극 효과를 바탕으로, 질량 전달 계수(α)는 양극 해리에 대한 Tafel 기울기에 의해서 결정되었다.

주제어: 음극과 양극전위, 전류밀도, 타펠, 분극, 분극감도

ABSTRACT. We measured the variations of potentials and current densities for several polymers. The results were carefully examined to identify various factors such as temperature and pH to influence the potential and rate. The Tafel slope for anodic dissolution was determined by the polarization effect under these conditions. The optimum conditions were established for each case. The second anodic current density peak and maximum current density were designated as the relative polarization sensitivity (I_p/I_c). The mass-transfer coefficient value (α) was determined by the Tafel slope for anodic dissolution on the basis of the polarization effect under optimum conditions.

Keywords: cathodic and anodic potential, current density, tafel, polarization, polarization sensitivity

INTRODUCTION

In response to the increasing concern over environmental issues,¹ the European Commission (EC), the administrative arm of the European Union (EU), will soon launch a consultation program examining the environmental issues related to poly(vinylchloride) (PVC). The EC has already adopted a green paper evaluating environmental aspects of PVC with the specific provisos that the consultation be based

on science and include aspects related to human health. The paper sets out details of the recent studies the EC has conducted in this area. It also invites discussions on two major areas: (1) the use of additives such as lead, cadmium, and phthalates; and (2) the waste management of PVC, including the options of recycling, incineration, and land fill disposal. The aim of this project is to give the EC the scientific basis to develop a comprehensive strategy on PVC in early 2001. The EC emphasizes that PVC

to be produced for practical applications will account for about 30% of the total production of plastic in Europe. The green paper is an "unsatisfactory review of the PVC life cycle" according to the assessment of the European Council of Vinyl Manufacturers.

Before Shirakawa, MacDiarmid, and Heeger made their seminal discovery in 1977, the idea of plastics being able to conduct electricity like metal seemed ludicrous for organic polymers known as insulators. However, these three researchers found that by doping a known conjugated polymer (polyacetylene) it could conduct a charge. Since then, scientists have synthesized a number of other conducting polymers as well as a host of related polymers that have semiconducting and light-emitting properties. Accordingly, the development of polymers has led to new types of organic materials that can combine the processing advantages and mechanical properties of plastics with electronic and optical properties of metals and inorganic semiconductors. Furthermore, these materials in turn have led to the development of organic and polymeric light-emitting diodes, field-effect transistors, and photovoltaic devices. For example, conducting polymers are being used as anti-static coatings and corrosion inhibitors, and even play "a major role as a radar-absorbing screen coating in stealth bombers", according to the chemistry professor Holmes, who directs the Melville Laboratory for polymer synthesis at the University of Cambridge. Professor Holmes

told Chemical and Engineer News (C & EN) that a light-emitting conducting polymer is now being included in mobile-phone displays. Other applications of conducting polymers that can soon emerge include light-weight batteries for cars, electromagnetic shielding, ultra-thin computer monitors and TV sets, artificial nerves, and sensors.³ However, no previous reports exists on the polarization of polymers. In this context, this paper will be the first attempt to correlate polarization tests performed by an electrolytic polarization method. In addition, we investigated the detailed influences of temperature and pH.

EXPERIMENTAL SECTION

Poly(ethyleneterephthalate) was purchased from the Aldrich Chemical Company. The electrolytic and polarizing measurements were performed in toluene or dimethylformamide (DMF). The supporting electrolyte was either tetrabutylammonium perchlorate or lithium perchlorate. The supporting-electrolyte concentration was typically 0.10 M. The electrode tip of the working-electrode system consisted of a 1 cm² piece of silver (0.1 mm thickness) as the conducting material, which, together with a silver wire, was sealed perpendicular to the rod (wire) axis for the electrical conduct. The reference electrode was a saturated calomel electrode (Ag/AgCl; Koslow Scientific Company, P/N 1004), a graphite carbon

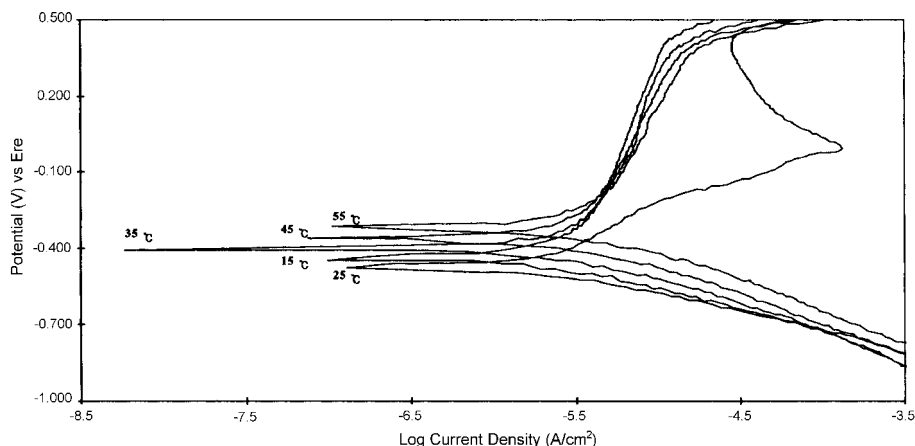


Fig. 1. Polarization curves of poly(carbonate) at various temperatures.

rod was used as the counter electrode, and the electrolysis cells were of the conventional design.

All experimental solutions were of typical 0.25% (w/v) in the redox-active species and deoxygenated by purging with prepurified nitrogen for at least 15 min. All experiments were performed at a scan rate of 7 mV/s on CMS 100 and 105 (Gamry Instruments, Inc). The Tafel plots were obtained from the -2.0 to +1.0 V region at a steady-state potential. The pH of the solution was adjusted by sodium hydroxide or hydrochloric acid.

RESULTS AND DISCUSSION

Fig. 1 shows the polarization curves for poly(carbonate) at 25 °C. These curves were obtained with three-step potentials and current densities. The redox potentials of the specimens were measured within the range of +2.0 V to 2.0 V versus SCE. The results are summarized in Table 1.

Effect of temperature. Fig. 2 shows the variations of potentials derived from the cathodic and anodic polarization curves. As shown in Fig's 2 and 3

Table 1. Parameters of temperature and pH for polymers [PVC(1), PET(2), PP(3), PC(4)]

Redox wave	Temperature (°C)					pH					
	15	25	35	45	55	3.0	5.0	7.0	9.0	11.0	
1st-wave	(1)	-0.80	-0.70	-0.70	-0.65	-0.65	-0.50	-0.50	-0.55	-0.50	-0.55
	(2)	-0.80	-0.70	-0.29	-0.24	-0.24	-0.21	-0.14	-0.25	-0.31	-0.39
	(3)	-0.58	-0.58	-0.47	-0.47	-0.47	-0.31	-0.37	-0.37	-0.24	-0.37
	(4)	-0.44	-0.47	-0.41	-0.36	-0.32	-0.48	-0.42	-0.46	-0.46	-0.46
2nd wave	(1)	0.22	0.11	0.08	0.08	0.28	0.08	0.08	0.12	0.12	0.12
	(2)	-0.60	-0.50	-0.09	-0.02	-0.04	0.00	0.00	0.00	0.00	0.00
	(3)	0.37	0.34	0.32	0.32	0.32	0.37	0.05	0.05	0.26	0.24
	(4)	0.43	0.41	0.40	0.38	0.39	0.00	0.11	0.12	0.14	0.15
3rd wave	(1)	0.47	0.37	0.33	0.33	0.62	0.50	0.50	0.57	0.55	0.54
	(2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	(3)	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.40	0.00	0.00
	(4)	0.00	0.00	0.00	0.00	0.00	0.43	0.43	0.40	0.44	0.44

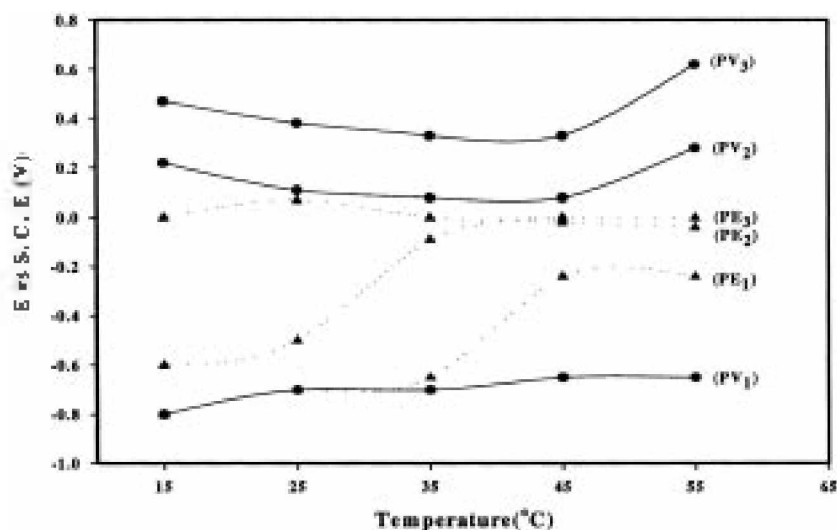


Fig. 2. Variation of potential as a function of temperature (°C).

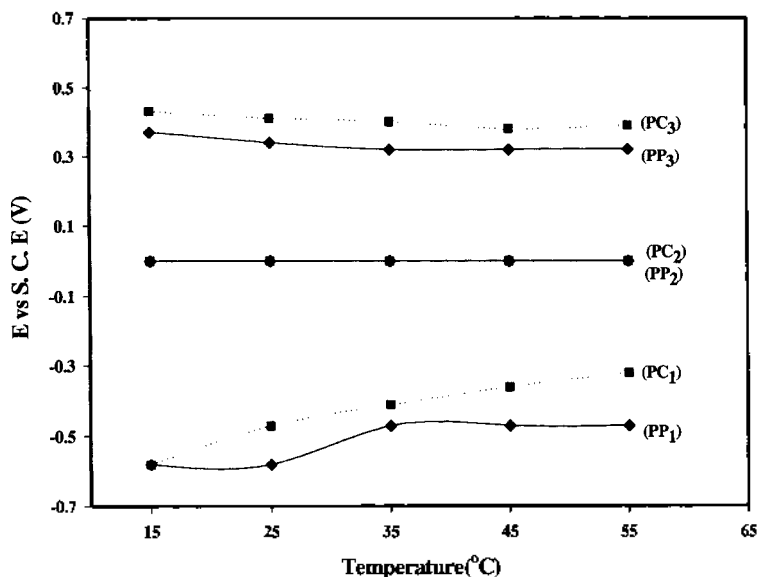


Fig. 3. Variation of potential as a function of temperature (°C): PPI-3: poly(propylene) waves; PCI-3: poly(carbonate) waves.

for polymers, poly(vinylchloride) (PVC), poly(ethyleneterephthalate) (PET), poly(propylene) (PP), and poly(carbonate) (PC), the potential efficiencies of the 1st wave and 2nd waves of PET are represented as the cathodic potentials, while the 2nd and 3rd waves were maintained at the anodic potentials at all temperatures.

Oxidations occur when the 2nd wave reaches 15 °C (PVC: $E=0.22$ V, PP: $E=0.37$ V; PC: $E=0.43$ V), 25 °C (PVC: $E=0.11$ V; PP: $E=0.34$ V; PC: $E=0.41$ V), 35 °C (PVC: $E=0.08$ V; PP: $E=0.32$ V; PC: $E=0.40$ V); 45 °C (PVC: $E=0.08$ V; PP: $E=0.32$ V; PC: $E=0.38$ V); and 55 °C (PVC: $E=0.28$ V; PP: $E=0.32$ V; PC: $E=0.39$ V). In addition, they also occur when the 3rd wave reaches 15 °C (PVC: $E=0.47$ V), 25 °C (PVC: $E=0.37$ V), 35 °C (PVC: $E=0.33$ V), 45 °C (PVC: $E=0.33$ V), and 55 °C (PVC: $E=0.62$ V). Especially, the potential efficiencies of the 3rd waves exhibit the anodic potentials for only PVC, whereas the PET, PP, and PC waves do not undergo redox reactions.

A series of polarity tests related to the 2nd waves exhibit lower potentials than those found for the oxidations of PVC (35~45 °C, PP (35~55 °C), and PC (45~55 °C). These results suggest that the high-

est-efficient temperature lies at lower reduction potentials rather than oxidation potentials. In particular for PVC, the best temperature range turned out to be in the range of 35~45 °C.

Effect of pH. Fig's 4 and 5 show the variations of potentials with pH values for the PVC, PET, PP, and PC polarization curves.³ The redox potential values for the 1st waves shifted to negative values. The curves of the 2nd and 3rd waves occur while oxygen is being consumed, and the 1st wave of the cathodic reaction results from the reduction of hydrogen ions in solution.

The oxidation-potential values have been measured for the 2nd and 3rd waves in various pH values. The oxidation potentials for the 2nd waves are as follows: (1) at pH=3.0: $E=0.08$ V (PVC), 0.00 V (PET), 0.37 V (PP), and 0.00 V (PC); (2) at pH=5.0: $E=0.08$ V (PVC), 0.00 V (PET), 0.05 V (PP), and 0.11 V (PC); (3) at pH 7.0: $E=0.12$ V (PVC), 0.00 V (PET), 0.05 V (PP), and 0.12 V (PC); (4) at pH 9.0: $E=0.12$ V (PVC), 0.00 V (PET), 0.26 V (PP), and 0.14 V (PC); (5) at pH=11.0: $E=0.12$ V (PVC), 0.00 V (PET), 0.24 V (PP), and 0.15 V (PC). In addition, the oxidation potentials for the 3rd waves are as follows: (1) at pH=3.0: $E=0.50$ V (PVC), 0.00 V (PET),

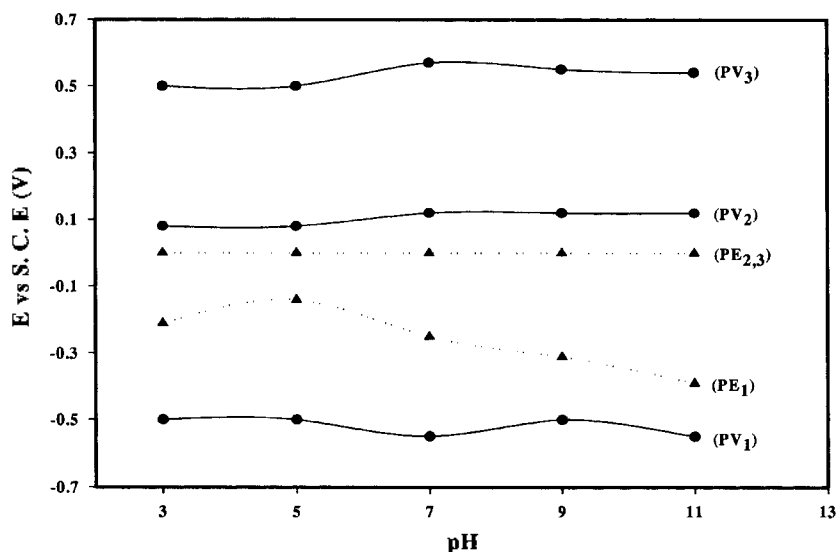


Fig. 4. Dependences of potential on pH: PV1-3: PVC waves; PE1-3: PET waves.

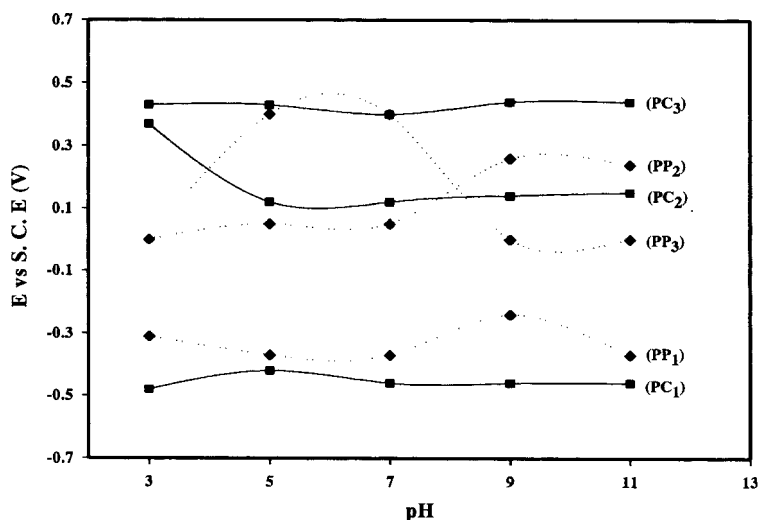
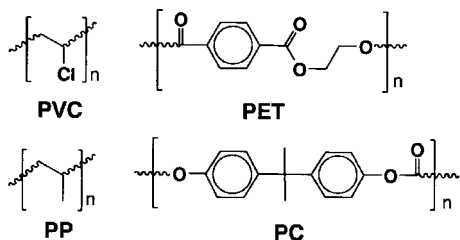


Fig. 5. Dependences of potential on pH: PP1-3: poly(propylene) waves; PC1-3: poly(carbonate) waves.

0.00 V (PP), and 0.43 V (PC); (2) at pH=5.0: $E=0.50$ V (PVC), 0.00 V (PET), 0.40 V (PP), and 0.43 V (PC); (3) at pH=7.0: $E=0.57$ V (PVC), 0.00 V (PET), 0.40 V (PP), and 0.40 V (PC); (4) at pH=9.0: $E=0.55$ V (PVC), 0.00 V (PET), 0.00 V (PP), and 0.44 V (PC); (5) at pH=11.0: $E=0.54$ V (PVC), 0.00 V (PET), $E=0.00$ V (PP), and 0.44 V (PC). Here, the negative potential values obtained from the 1st waves correspond to reduction processes.

A series of oxidation tests for the 2nd and 3rd waves indicate the lowest oxidation potentials of polymers to lie in pH=3.0~5.0 {PVC₂ ($E=0.08$ V) and PVC₁ ($E=0.50$ V)}, and also in pH 5.0~7.0 {PP₂ ($E=0.05$ V), PP₁ ($E=0.40$ V), PC₂ ($E=0.11$ ~0.12 V), and PC₁ ($E=0.43$ ~0.40 V)}. These results suggest that the fast oxidation reactions corresponding to the 2nd and 3rd waves of all specimens occur in the range of pH=3.0~5.0 for PVC. On the other hand,

any oxidation potential cannot be observed in the 2nd wave for PET. Moreover, the oxidations of PP and PC take place in the range of pH=5.0~7.0. Therefore, corrosion can be expected to readily occur in acidic rather than basic solutions. Structures of the polymers in this study are shown below.



The redox potentials seem to be related to the number of benzene rings in polymers. For example, the electrochemical reaction occurs rapidly in the absence of the benzene ring. For PET and PC, the number of the benzene rings appears to play a role, and the polymer containing one benzene ring oxidizes more rapidly than one containing two benzene rings.

Resistances and rates. The impedance response is related to the dissociation from the charge-transfer process and is given as the product of the interfacial charge-transfer resistances. Electrolytic techniques such as linear polarization can be used for the rapid measurement of polarization resistances.⁴ Table 2 shows the data from our experiments. Polarization resistance (R_p) and rate (mm/y) can be presented by linear polarization curves.^{5,6} The value of resistance ($\text{K}\Omega\text{cm}^2$)⁷ and rate (mm/y)⁸ were obtained from a

Tafel plot, and the resistance was obtained from the following equation:

$$R_p = \Delta E / \Delta i = (\beta_A \beta_c) / [2.30 I_{\text{corr}} (\beta_A + \beta_c)]$$

Where R_p is a polarization resistance, ΔE is a potential difference, Δi is a current difference, β_A is an anodic Tafel constant, and β_c is a cathodic Tafel constant.

$$\text{Rate} = (0.13 I_{\text{corr}} E_q H) / d$$

where d is the sample density (g cm^3), and $E_q H^-$ -equivalent weight (g).

These values are obtained from the slopes at E_{oxi} of a plot of I versus E in the region of E_{oxi} . The Tafel method is a useful device for evaluating kinetic parameters. The anodic branch with a slope $(1-\alpha)nF/2.3RT$ was used to obtain the mass transfer coefficients (α). The values (α) obtained, as summarized in Table 2, are higher than 0.50. Accordingly, the electrode reaction seems to be reversible under all conditions.^{9,10} The Tafel slope for the anodic dissolution was determined by evaluating the effects of pH and temperature on polarization. All polymers exhibit a transition in the electrolytes, and the slopes representing the anode dissolutions shift slightly in the potential direction depending on temperatures (15, 25, 35, 45, and 55 °C).

Table 2 shows the variations in the redox resistances and rates under various conditions. These have been determined from the optimum potential effects of pH and temperature. As expected, the oxidation rate is the highest for the lowest resistance. In contrast, temperature and salt give a bal-

Table 2. Effects of various conditions on polarization characteristics for polymers [PVC(1), PET(2), PP(3), PC(4)]

Conditions	Parameters					
	Optimum (°C)	Potential E (V)	Resistance ($\text{K}\Omega\text{cm}^2$)	Rate (mm/y)	Reversibility (α)	Susceptibility (I_i/I_c)
Temperature	(1) 30	0.33	1.56	123.43	0.98	0.82
	(2) 25	0.07	3.05	1.38	0.98	0.41
	(3) 35	0.38	66.7	0.07	0.60	0.65
	(4) 45	0.38	25.6	0.23	0.70	0.74
pH	(1) 3.0	0.50	0.93	63.08	0.97	0.82
	(2) 4.0	-0.14	1.80	2.56	0.97	0.47
	(3) 5.0	0.05	14.90	0.64	0.87	0.75
	(4) 5.0	0.11	7.10	0.69	0.53	0.68

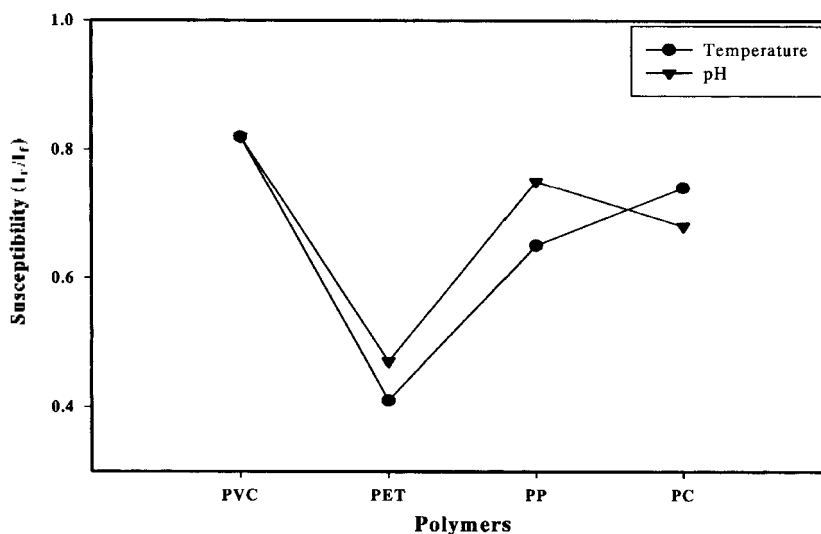


Fig. 6. Sensitivity effects of maximum current density for forward and reverse scans.

anced relationship between resistance and oxidation rate. The optimum condition of resistance and rate depend on the time of exposure.¹¹

Effect of current density. Fig. 6 shows variations of the current density ratios between a reverse current (I_r) and a forward current (I_f). The susceptibility has been obtained from the ratio of I_r to that of I_f . As shown in Fig. 6, the oxidation susceptibility appears to be in the order of PVC>PP>PC>PET depending on temperatures and in the order of PVC>PC>PP>PET for pH values. These results cannot be explained on the basis of oxidation, and they would appear to result from an increase in the current density probably due to another factor.

CONCLUSIONS

The polarization curves of poly(ethyleneterephthalate) in a nonaqueous solvent showed two or three redox waves. The 1st wave corresponds to reduction at all temperatures. The optimum temperatures for oxidation seem to be 30 °C (PVC), 25 °C (PET), 35 °C (PP), and 45 °C (PC), and the optimum pH values appear to be 3.0 (PVC), 4.0 (PET), 5.0 (PP and PC). The oxidation of the polymer is expected to occur readily in an acidic solution, and oxidation potential appears to be related to the num-

ber of benzene rings present in the polymer. The electrode reaction seems to be reversible under all conditions.

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