

Network Formation in Poly(ethylene Terephthalate) by Thermooxidative Degradation

KENTARO YODA, AKIO TSUBOI, MINORU WADA, and
REIZO YAMADERA, *Katata Research Institute, Toyobo Company,
Ltd., Honkatata, Ohtsu, Japan*

Synopsis

Gelation of poly(ethylene terephthalate) by heating at 263°–300°C was investigated. Under nitrogen flow, crosslinks were scarcely formed. However in air, degradation and crosslinking were common, and these were accelerated by purging gaseous and sublimable degradation products out of the system with a stream of air. The main component of the sublimate was terephthalic acid. Infusible and insoluble gel was treated with methanol at 260°C, and then the methanolysis products were separated into two parts. The methanol-insoluble part exhibited a polyene structure with ester groups, and the methanol-soluble part contained dimethyl terephthalate, ethylene glycol, and some 1,2,4-butanetriol. To clarify the relation between the crosslinking and the formation of vinyl ester groups, the degradation of vinyl methyl terephthalate was studied. Thermooxidative degradation of linear polyesters other than poly(ethylene terephthalate) was also studied. Poly(ethylene isophthalate) and poly(ethylene sebacate) were easily gelated. However, poly(trimethylene terephthalate) and poly(neopentyl terephthalate) were scarcely gelated. The primary reaction leading to crosslinking is assumed as follows. At first, the random scission of polyester chain may take place forming carboxylic acids, vinyl esters, aldehydes, etc. After accumulation of vinyl esters to some extent, vinyl polymerization of the esters takes place and network structures are formed.

INTRODUCTION

Many investigations¹ have been carried out on the degradation of poly(ethylene terephthalate) and many useful results have been obtained for the interpretation of the reaction mechanism.

The possibility of branching or crosslinking in poly(ethylene terephthalate) by heating has been suggested,² and Hoffrichter³ reported the presence of a gel-like material in the knob found in commercial polyester filament. This gel-like material seems to be formed by thermal or thermooxidative degradation during melt spinning.

The present paper will be concerned with the crosslinking of poly(ethylene terephthalate) by heating in air at the temperature range from 263°C to 300°C. Furthermore, in order to ascertain the structures of the network and the mechanisms of crosslinking reaction, results of chromatographic analysis and model reactions are shown.

RESULTS AND DISCUSSION

Degradation and Crosslinking of Poly(ethylene Terephthalate) by Heating

Dry poly(ethylene terephthalate) powder was placed uniformly in a stainless steel tray of 20-cm² cross area and heated at a given temperature for a definite time in the apparatus shown in Figure 1. Air or nitrogen was passed through the vessel as needed.

The weight loss of sample by heating was determined, and 100 mg of degraded material was dissolved in 25 ml of *o*-chlorophenol at 80°C. Insoluble gel was collected and extracted with acetone for 4 hr, and gel was dried at 80°C under reduced pressure. This insoluble gel fraction had no melting point and was swollen with *o*-chlorophenol, trifluoroacetic acid, and concentrated sulfuric acid. Differential scanning calorimetry (DSC) curve of the gel is shown in Figure 2 as a typical example, in comparison to that of poly(ethylene terephthalate).

The weight loss and percent of gel fraction by heating poly(ethylene terephthalate) under various conditions are given in Tables I to III. Under nitrogen flow, gel structure was scarcely formed; however, degradation and crosslinking proceeded in air and were especially accelerated by

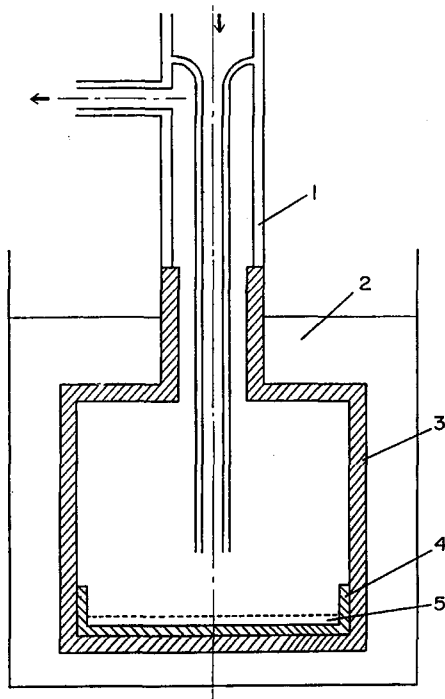


Fig. 1. Schematic representation of apparatus for degradation: (1) glass tube; (2) salt bath; (3) stainless steel oven; (4) stainless steel tray; (5) polyester sample.

purging gaseous and sublimable degradation products out of the system with a stream of air. Degradation was also affected by the amount of starting sample, in other words, by the thickness of the sample layer. The reduction of the thickness of sample layer resulted in extensive degradation and gel formation.

Figure 3 shows the correlation between the percent of gel fraction and the weight loss by heating. The influence of inorganic materials included

TABLE I
Degradation of Poly(ethylene Terephthalate) in
Nitrogen at 300°C^a

Polycondensation catalyst	Catalyst concn, wt-%	Polymer weight loss, %	Gel, %
Zn(OAc) ₂ ·2H ₂ O	0.036		
Sb ₂ O ₃	0.025	5.8	0
Zn(OAc) ₂ ·2H ₂ O	0.036		
GeO ₂	0.01	2.8	0
Ca(OAc) ₂ ·H ₂ O	0.10		
Sb ₂ O ₃	0.025	3.8	0
Ca(OAc) ₂ ·H ₂ O	0.10		
GeO ₂	0.01	4.0	0
Mn(OAc) ₂ ·4H ₂ O	0.04		
Sb ₂ O ₃	0.025	4.6	0
Mn(OAc) ₂ ·4H ₂ O	0.04		
GeO ₂	0.01	4.0	0

^a Weight of sample, 1 g; flow rate of nitrogen, 800 ml/min; time, 4 hr.

TABLE II
Degradation of Poly(ethylene Terephthalate) in Air at 300°C

Polycondensation catalyst	Catalyst concn, wt-%	Sample weight, g	Degradation time, hr	Polymer weight loss, %	Gel, %
Zn(OAc) ₂ ·2H ₂ O	0.036				
Sb ₂ O ₃	0.025	1.0	4	4.9	0.1
Zn(OAc) ₂ ·2H ₂ O	0.036				
Sb ₂ O ₃	0.025	1.0	4	7.3	0.8
Zn(OAc) ₂ ·2H ₂ O	0.036				
Sb ₂ O ₃	0.025	1.0	20	28.3	16.7
Zn(OAc) ₂ ·2H ₂ O	0.036				
Sb ₂ O ₃	0.025	0.5	4	13.8	0.7
Zn(OAc) ₂ ·2H ₂ O	0.036				
GeO ₂	0.01	1.0	4	3.8	0.6
Ca(OAc) ₂ ·H ₂ O	0.10				
Sb ₂ O ₃	0.025	1.0	4	5.6	0.6
Ca(OAc) ₂ ·H ₂ O	0.10				
GeO ₂	0.01	1.0	4	5.4	0.7
Mn(OAc) ₂ ·4H ₂ O	0.04				
Sb ₂ O ₃	0.025	1.0	4	4.2	0
Mn(OAc) ₂ ·4H ₂ O	0.04				
GeO ₂	0.01	1.0	4	4.2	0

TABLE III
 Degradation of Poly(ethylene Terephthalate) Under a Stream of Air^a

No.	Polycondensation catalyst	Catalyst concn, wt-%	Degradation		Polymer weight loss, %	Gel, %
			temp, °C	time hr		
1	Zn(OAc) ₂ ·2H ₂ O	0.036	300	0.5	4.5	0
	Sb ₂ O ₃	0.025				
2	Zn(OAc) ₂ ·2H ₂ O	0.036	300	1.0	12.5	2.0
	Sb ₂ O ₃	0.025				
3	Zn(OAc) ₂ ·2H ₂ O	0.036	300	1.5	15.8	5.0
	Sb ₂ O ₃	0.025				
4	Zn(OAc) ₂ ·2H ₂ O	0.036	300	2.0	16.6	5.5
	Sb ₂ O ₃	0.025				
5	Zn(OAc) ₂ ·2H ₂ O	0.036	300	3.0	31.3	26.6
	Sb ₂ O ₃	0.025				
6	Zn(OAc) ₂ ·2H ₂ O	0.036	300	4.0	34.0	50.0
	Sb ₂ O ₃	0.025				
7	Zn(OAc) ₂ ·2H ₂ O	0.036	300	6.0	39.3	80.1
	Sb ₂ O ₃	0.025				
8	Zn(OAc) ₂ ·2H ₂ O	0.036	280	4.0	29.6	38.5
	Sb ₂ O ₃	0.025				
9	Zn(OAc) ₂ ·2H ₂ O	0.036	263	4.0	22.3	4.8
	Sb ₂ O ₃	0.025				
10	Zn(OAc) ₂ ·2H ₂ O	0.036	300	4.0	28.7	48.2
	GeO ₂	0.01				
11	Ca(OAc) ₂ ·H ₂ O	0.10	300	4.0	29.6	42.5
	Sb ₂ O ₃	0.025				
12	Ca(OAc) ₂ ·H ₂ O	0.10	300	4.0	28.8	33.8
	GeO ₂	0.01				
13	Mn(OAc) ₂ ·4H ₂ O	0.04	300	4.0	27.3	35.0
	Sb ₂ O ₃	0.025				
14	Mn(OAc) ₂ ·4H ₂ O	0.04	300	4.0	25.6	20.5
	GeO ₂	0.01				
15	Zn(OAc) ₂ ·2H ₂ O	0.036	300	2.0	30.1	50.1
	Sb ₂ O ₃	0.025				
16	Zn(OAc) ₂ ·2H ₂ O	0.036	300	2.0	29.6	50.4
	GeO ₂	0.01				

^a Weight of sample: Nos. 1-14: 1 g; Nos. 15, 16: 0.5 g; flow rate of air, 800 ml/min.

in poly(ethylene terephthalate), which were used as catalyst in the polymerization, was not significant. The magnitude of the influence of these inorganic catalysts on promoting gelation seems to increase in the following order: transesterification catalyst, Mn, Ca < Zn; polycondensation catalyst, Ge < Sb.

One of the most striking observations made in the study of thermooxidative degradation of poly(ethylene terephthalate) is that both degradation and crosslinking occur.

One gram of poly(ethylene terephthalate) powder was heated at 300°C. under a stream of air (800 ml/min) in the apparatus shown in Figure 1. The experimental results of the degradation are collected in Figures 4 and

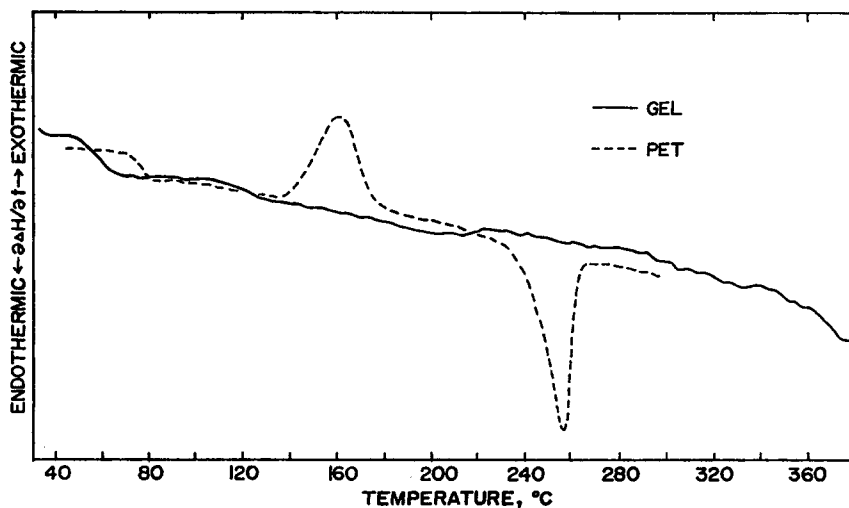


Fig. 2. DSC curve of gel, compared with that of poly(ethylene terephthalate).

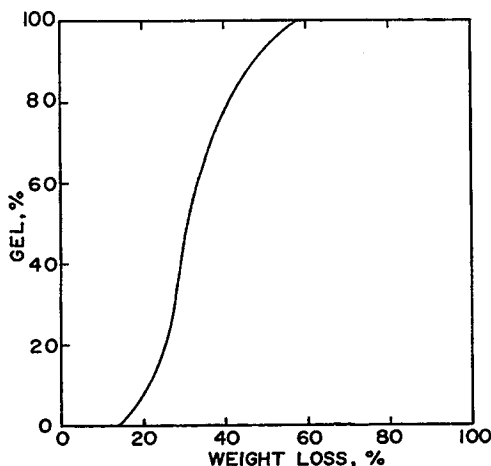


Fig. 3. Correlation between per cent of gel fraction and weight loss.

5. Figure 4 shows the plots of weight loss, acid value, and gel percent versus degradation time. Figure 5 gives the relation of the intrinsic viscosity and the Huggins' viscosity parameter k' of the sol fraction with degradation time in the same experiment as Figure 4. The decomposition reaction took place as a consequence of heating, and it induced discoloration and decreased intrinsic viscosity. As poly(ethylene terephthalate) degraded, its color changed gradually from yellow to brown. At first, chain scission proceeded preferentially, but after 30 min the crosslinking was predominant. It is probable that the increase in k' value with degradation time depends on the structural change of the polymer molecules such as branching or crosslinking.

It has been shown theoretically⁴ that when fractures and crosslinks are introduced at a uniform rate into linear polymer molecules with a random distribution of lengths, the sol fraction S may be related to time as follows:

$$S + S^{1/2} = p \cdot q^{-1} + (q \cdot u \cdot t)^{-1} \quad (1)$$

where p and q are the probabilities that a repeating unit is fractured and crosslinked, respectively, in unit time, and u is the average number of repeating units per molecule at time $t = 0$.

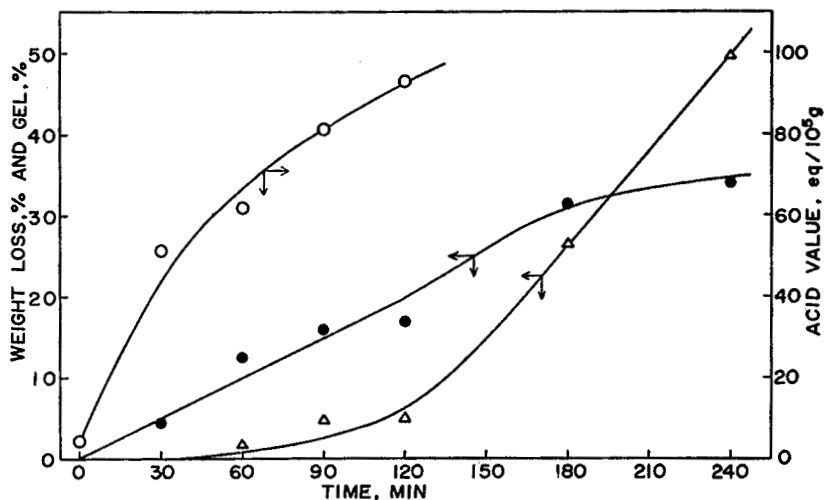


Fig. 4. Time dependence of weight loss, acid value, and per cent of gel fraction: (○) acid value; (●) weight loss; (△) gel per cent.

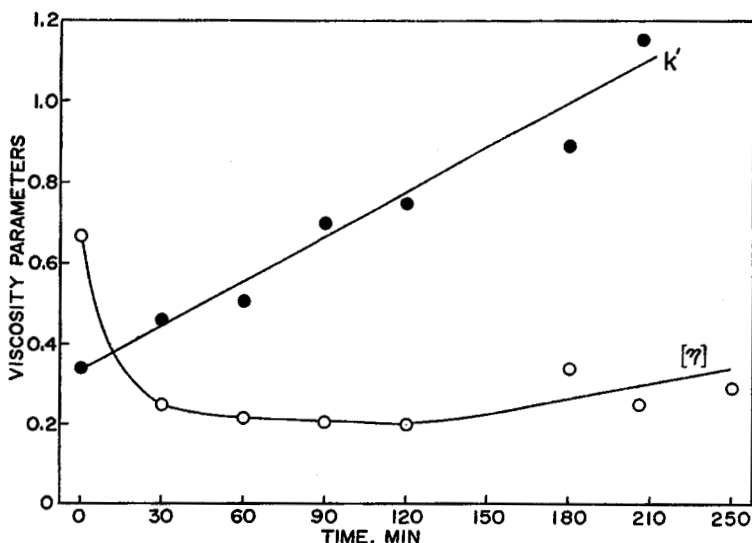


Fig. 5. Variation of intrinsic viscosity and Huggins' viscosity parameter k' of sol fraction with degradation time: (○) intrinsic viscosity; (●) k' .

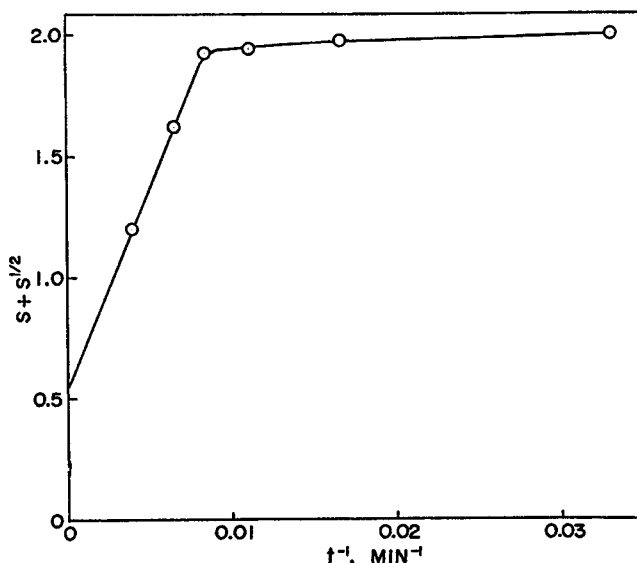


Fig. 6. Plot of $S + S^{1/2}$ vs. reciprocal of heating time.

In Figure 6, $S + S^{1/2}$ is plotted against the reciprocal of time of heating. Gelation seems to take place predominantly when t^{-1} is less than 0.01. This suggests a process in which chain scission takes place first, and subsequently crosslinks are gradually formed. That is, it is to be expected that the degradation products take part in the crosslinking reactions.

Sublimates from Poly(ethylene Terephthalate) Melt During Thermo-oxidative Degradation

When poly(ethylene terephthalate) was subjected to thermo-oxidative degradation at 300°C, sublimable materials evolved and attached themselves to the reaction vessel, separating into two parts. Most of the sublimates (A) attached at the lower part, while at the upper part a small amount of white crystalline material (B) attached.

Fraction B was easily soluble in acetone, ether, chloroform, etc., and melted around 170°–173°C. Figure 7 shows the infrared spectrum of B. The band at 1790 cm^{-1} is probably attributable to acid anhydride. The bands at 1690 cm^{-1} and 1280 cm^{-1} are due to carboxylic acid. This material is not a pure compound, judging from its melting range.

The insoluble part of fraction A in ammoniacal water melted at 334°C; from its infrared spectrum (Fig. 8) and elemental analysis (C, 62.34%; H, 4.28%) it is the cyclic trimer of ethylene terephthalate. In the part of fraction A that was soluble in ammonia, about 0.2 wt-% of terephthalaldehydic acid was detected by polarographic analysis.

The extraction residue of A by acetone was shown to be terephthalic acid by infrared spectrum and elemental analysis (C, 57.98%; H, 3.97%). The acetone-soluble part of A should be a mixture of linear oligomers of

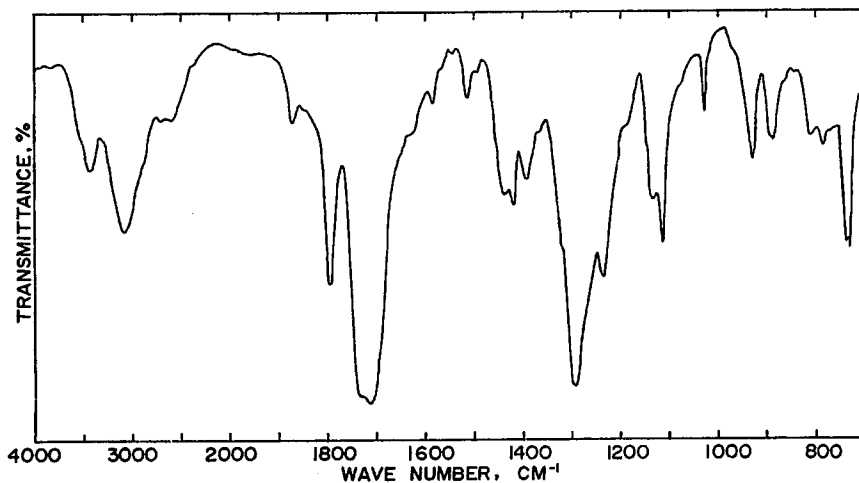


Fig. 7. Infrared spectrum of sublimate B.

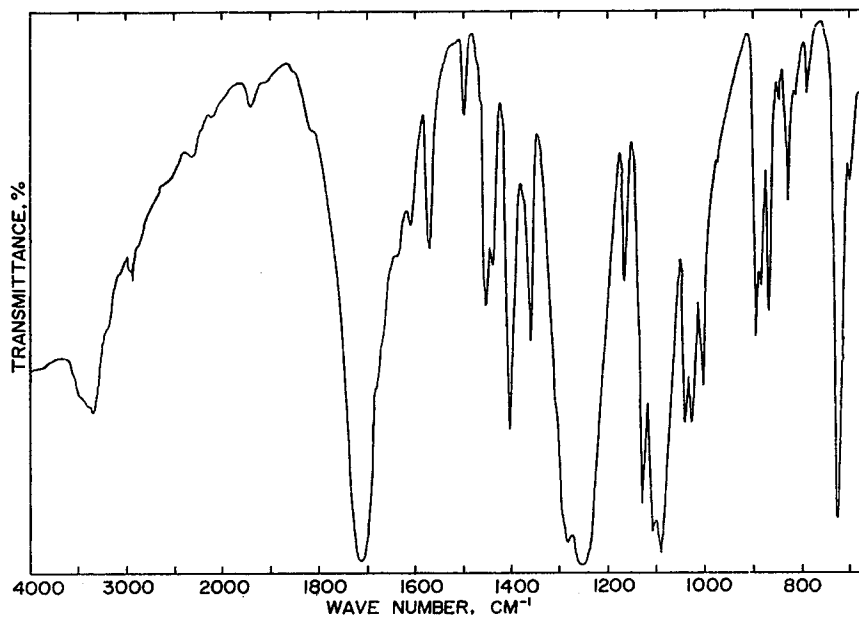


Fig. 8. Infrared spectrum of insoluble part of sublimate A in ammoniacal water.

poly(ethylene terephthalate) mainly composed of monohydroxyethyl terephthalate.⁵

Next, a mixture of A and B was treated with methanol at 260°C, and the presence of dimethyl terephthalate, ethylene glycol, and terephthalaldehydic acid methyl ester was shown by gas-chromatographic analysis of the methanolized solution, as shown in Figure 9.

From the above results, it is evident that the main component of the sublimate is terephthalic acid.

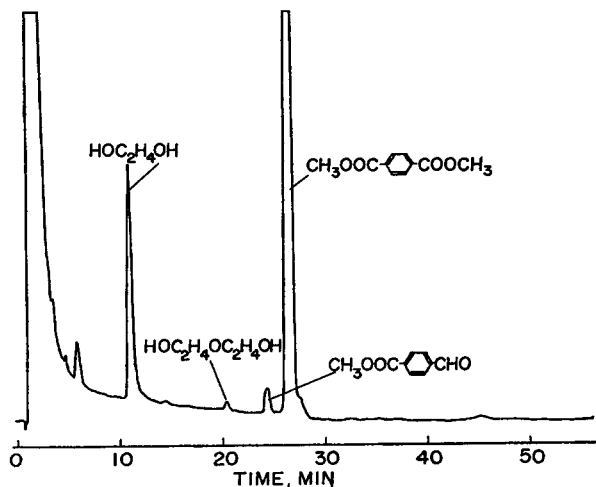


Fig. 9. Gas chromatogram of the methanolysis product of a mixture of sublimates A and B: column temperature, $100^\circ\text{--}200^\circ\text{C}$ ($4^\circ\text{C}/\text{min}$); carrier gas, He.

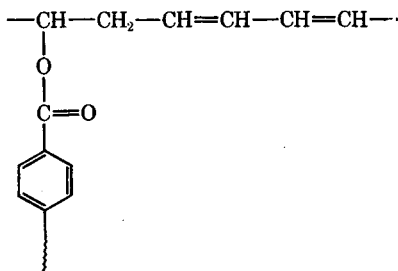
Chemical Analysis of Gel

The infusible and insoluble gel was treated with an excess of methanol at 260°C , and the decomposition product were separated into two parts; one was methanol soluble and the other, methanol insoluble.

The methanol-insoluble part was a brown-black powder and was insoluble in ordinary organic solvents but soluble in *o*-chlorophenol, trifluoroacetic acid, and concentrated sulfuric acid. The methanol-insoluble part was washed with acetone and dried. It was about 0.5–1.0 wt-% of the gel (C, 62.75%; H, 3.44%).

The ultraviolet absorption spectrum of this material in concentrated sulfuric acid showed an absorption peak at $300\text{ m}\mu$. Figure 10a shows the infrared spectrum of the methanol-insoluble part. The broad band at 1600 cm^{-1} is probably due to conjugated double bonds. In addition, bands based on ester carbonyl (1720 cm^{-1} , 1280 cm^{-1}) are also found.

It should be noted that this infrared spectrum is very similar to that of the thermo-oxidative degradation product of poly(vinyl methyl terephthalate) (Fig. 10b). With respect to this point, more detailed discussion will be given in a later section. From the above results, it is probable that the methanol-insoluble part has the following structure, which was presented by Zimmermann⁶:



The methanol-soluble part was concentrated to an appropriate quantity and subjected to gas-chromatographic analysis. The chromatogram of the methanol-soluble part is shown in Figure 11. Figure 12 shows the chromatogram of the methanolysis product of a sample which was prepared by heating poly(ethylene terephthalate) at 300°C for 4 hr in air without gelation.

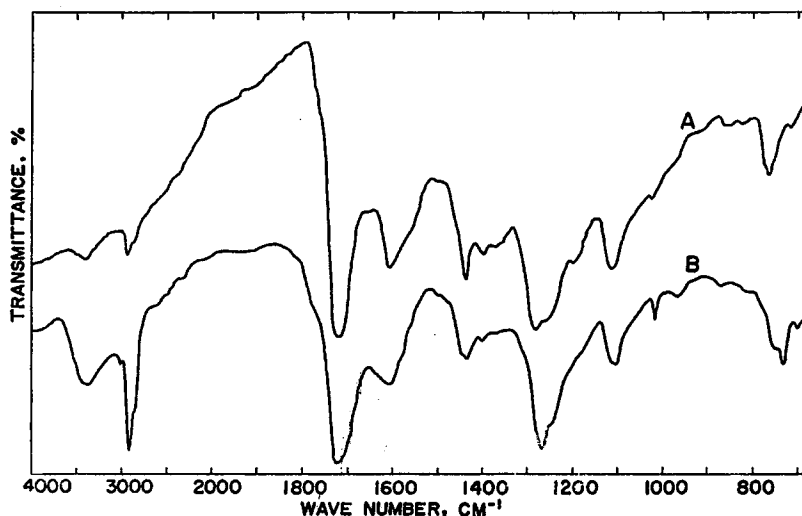


Fig. 10. (A) Infrared spectrum of the methanol-insoluble part of the methanolysis products of the gel. (B) Infrared spectrum of thermo-oxidation product of poly(vinyl methyl terephthalate).

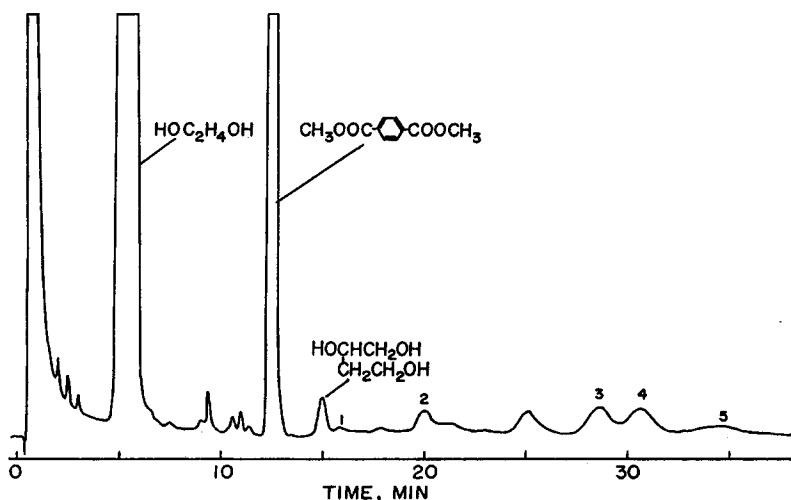


Fig. 11. Gas chromatogram of the methanol-soluble part of methanolysis products of the gel: column temperature, 100°–200°C (4°C/min); carrier gas, He.

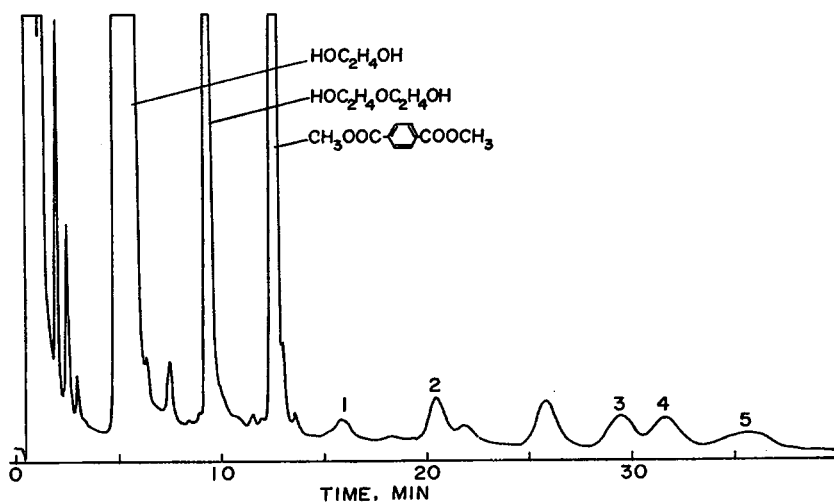


Fig. 12. Gas chromatogram of the methanolysis product of degraded poly(ethylene terephthalate) at 300°C in air (not gelled).

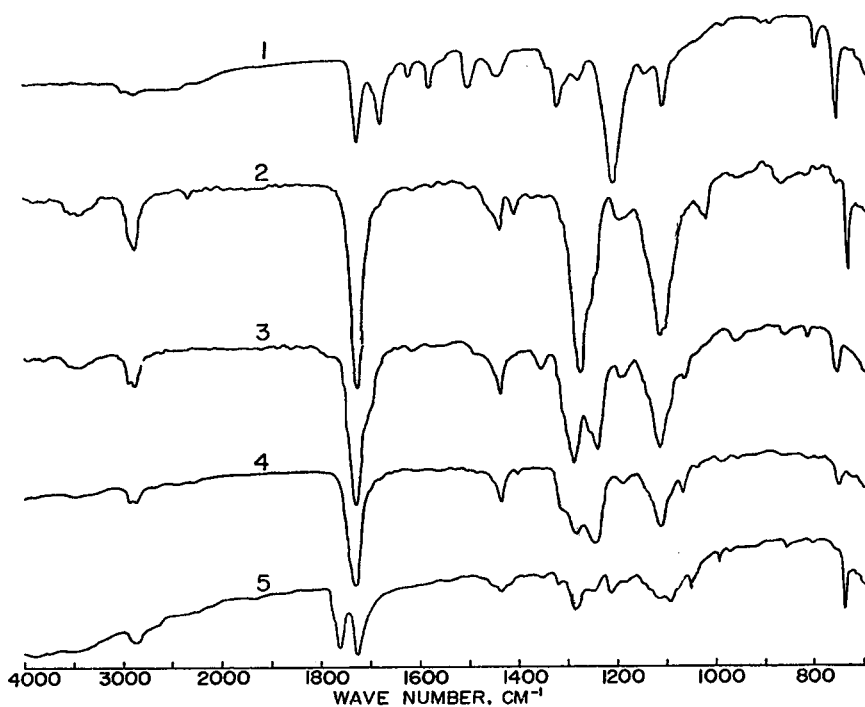


Fig. 13. Infrared spectra of the corresponding fractions for peaks 1-5 in Figures 11 and 12.

On comparing the two chromatograms, it is obvious that the diethylene glycol unit is scarcely contained in the gelated sample, whereas 1,2,4-butanetriol is present.

It is evident that the main components of the methanol-soluble part are dimethyl terephthalate and ethylene glycol. The components of peaks 1-5 in Figures 11 and 12 were not identified, but the infrared spectra of the corresponding fractions for each peak are shown in Figure 13.

No erythritol could be detected in the methanol-soluble part by gas-liquid chromatography operated at 200°C or thin-layer chromatography.

Model Reaction

To clarify the relation between gelation and the formation of vinyl ester groups, the degradation of vinyl methyl terephthalate was studied as a model reaction.

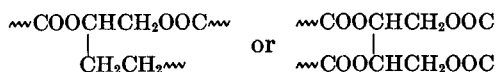
When vinyl methyl terephthalate was heated at 280°C in air, both sublimation and vinyl polymerization occurred prior to the decomposition. Therefore, to avoid complication, poly(vinyl methyl terephthalate) was synthesized at first, and then thermooxidative degradation of the polymer was studied.

Figure 14 shows the thermogravimetric analysis curve of poly(vinyl methyl terephthalate). The polymer decomposes mostly by 300°C. Thermooxidative degradation of poly(vinyl methyl terephthalate) was carried out at 300°C for 2 hr under a stream of air in the apparatus as already shown in Figure 1. A white sublimate deposited at the upper part of the apparatus in consequence of degradation reaction. The sublimate was confirmed to be monomethyl terephthalate by thin-layer chromatography, infrared spectroscopy, and elemental analysis. The residue of decomposition was a brown-black powder (C, 81.6%; H, 6.15%), and its infrared spectrum is shown in Figure 10*b*. The main reaction in the degradation of poly(vinyl methyl terephthalate) should be β -elimination to give olefinic double bonds and monomethyl terephthalate.

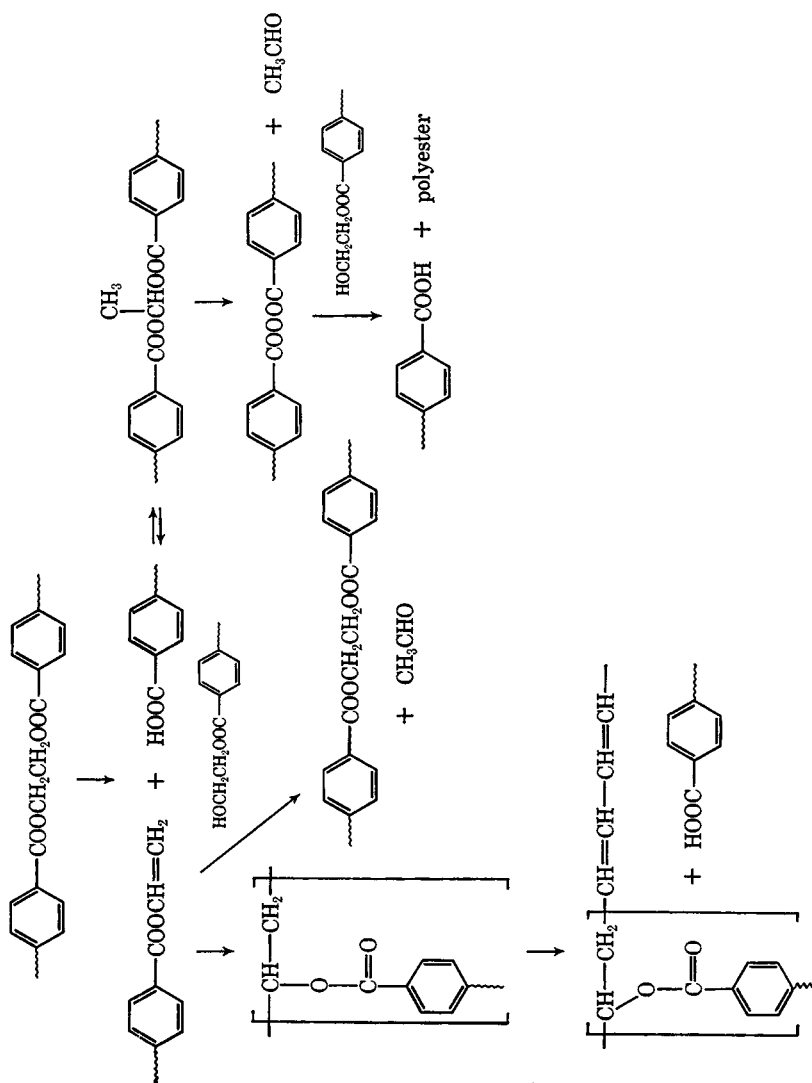
The similarity of the two infrared spectra in Figure 10 suggest that the gel of poly(ethylene terephthalate) has a structure similar to that of the decomposition product of poly(vinyl methyl terephthalate).

Mechanisms of Crosslinking

Sobue and Kajiura² have investigated the thermal degradation of poly(ethylene terephthalate) in vacuo and have suggested that branching or crosslinking was formed during the thermal degradation. They proposed the following structures for the branching or crosslinking formed:



Zimmermann and co-workers⁶ summarized the main reactions in the thermal degradation^{7,8} of poly(ethylene terephthalate) as follows:



Moreover, according to the recent investigation by Ozawa,⁹ the formation of many vinyl esters has been suggested by means of mass-spectrometric

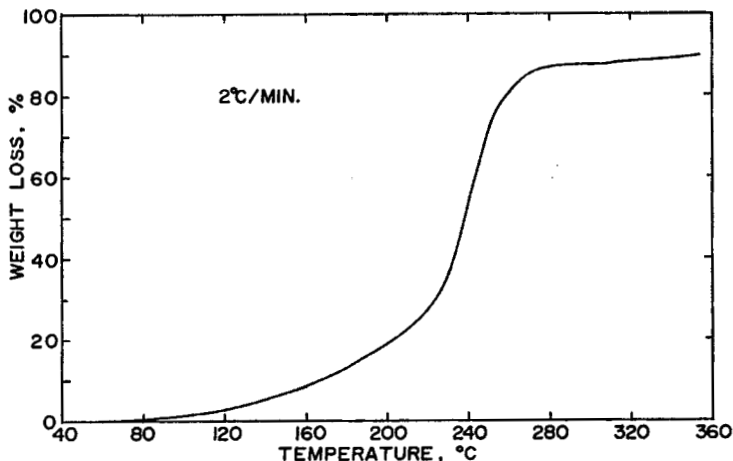
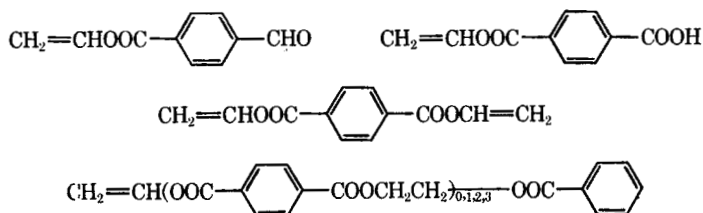
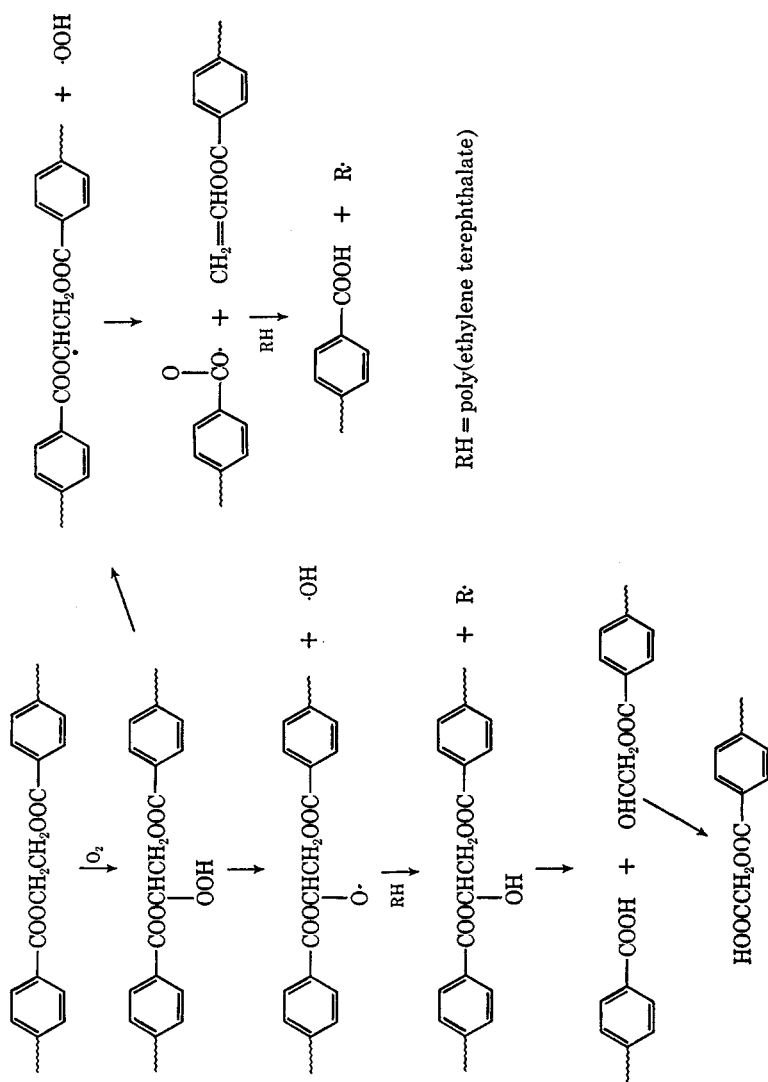


Fig. 14. Thermogravimetric analysis curve of poly(vinyl methyl terephthalate) (2°C/min).

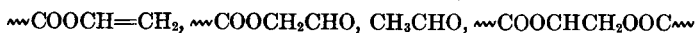
thermal analysis and thermogravimetric analysis of poly(ethylene terephthalate) under vacuum. He reported the following vinyl esters:



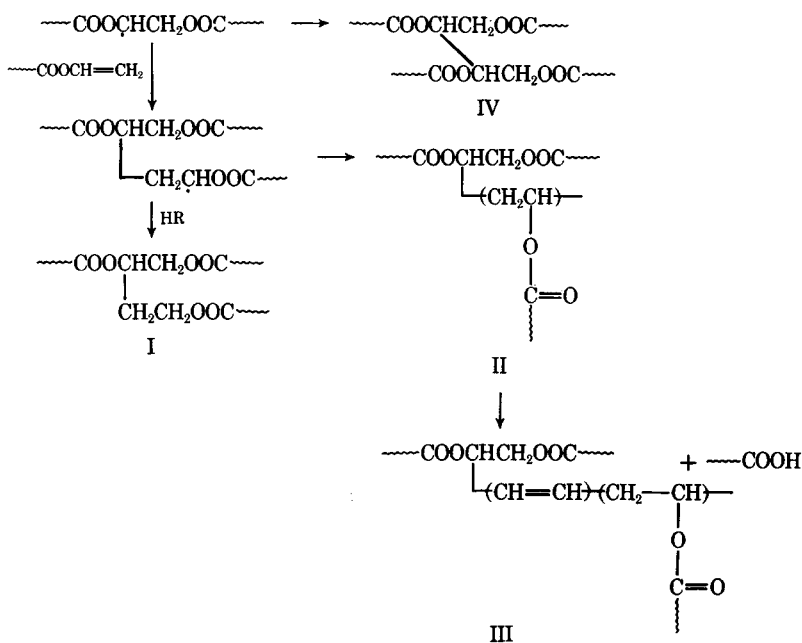
With regard to the thermo-oxidative degradation of poly(ethylene terephthalate), Buxbaum¹⁰ and Mikhailov¹¹ studied the degradation of poly(ethylene terephthalate) in the presence of oxygen. Buxbaum proposed the following scheme for the thermo-oxidative degradation of poly(ethylene terephthalate):



Among these degradation products, the following species may be taken as chemical species which can be a crosslinking unit:



In the first place, vinyl esters may be taken into consideration. One may consider the following three possible mechanisms involving the crosslinking reaction with regard to vinyl esters:



In addition to the detection of 1,2,4-butanetriol in the methanolized products of the gel, a substance with a similar structure to III was also founded in the gel part. Therefore, it is evident that vinyl esters play an important role in the formation of the gel. As erythritol was not detected in the methanolized products of the gel, the formation of structure IV by radical coupling may hardly take place in the experimental condition of the present study.

Next, the action of aldehydes on the formation of branching or crosslinking structure should be considered.

It is well known that aldehyde forms an acetal linkage with alcohol. Further, Goodings¹² assumes the formation of polyenaldehydes from acetaldehyde for the discoloration in poly(ethylene terephthalate). These polyenaldehydes may also be crosslinking components. It is an important problem to know whether or not there exists any direct relation between the formation of acetal linkage or polyenaldehyde and gelation.

In order to clarify the effect of aldehyde on gelation, terephthalaldehydic acid was used. Poly(ethylene terephthalate) was synthesized from bis(β -hydroxyethyl)terephthalate by melt state polycondensation. When 10% of terephthalaldehydic acid was added, the resultant polyester showed

The thermo-oxidative degradation of polyesters is very complicated reaction and, therefore, the mechanism of gelation is also a complicated one. It is imaginable that the tendency in gelation of linear polyesters depends on their chemical structures, molecular weights, etc. Linear polyesters other than poly(ethylene terephthalate) also formed a gel by thermo-oxidative degradation.

TABLE IV
Thermo-oxidative Degradation of Polyesters*

Polymer	Degradation		Polymer weight loss, %	Gel, %
	temp, °C	time, hr		
Poly(ethylene terephthalate)	300	4	31.2	52.6
Poly(ethylene terephthalate)	280	4	29.6	38.5
Poly(ethylene isophthalate)	300	4	40.9	49.2
Poly(ethylene sebacate)	300	4	27.2	22.4
Poly(neopentyl terephthalate)	280	4	29.6	1.9
Poly(trimethylene terephthalate)	280	4	52.3	3.9

* Weight of sample, 1 g; flow rate of air, 800 ml/min.

Further research is necessary, but preliminary experimental results are shown in Table IV. It can be noted that replacement of the protons on the β -carbon of $-\text{COOCH}_2\text{CH}_2-$ by methyl groups decreases gelation.

EXPERIMENTAL

Poly(ethylene terephthalate) was prepared from dimethyl terephthalate and ethylene glycol in the presence of inorganic materials as catalysts. The intrinsic viscosity of the polymers was about 0.61–0.63. Poly(ethylene sebacate), poly(trimethylene terephthalate) and poly(neopentyl terephthalate) were prepared from the corresponding acid and glycol by direct esterification followed by catalytic polycondensation.

Vinyl methyl terephthalate was prepared by the following method. To a mixture of 50 g of monomethyl terephthalate, 300 g of vinyl acetate, and 1.25 g of mercuric acetate, 0.36 g of concentrated sulfuric acid was added dropwise with stirring at 60°C. Then the mixture was refluxed for 1 hr. After the reaction mixture was maintained at 70°C for 70 hr with stirring, 0.5 g of sodium acetate was added. The excess or vinyl acetate and acetic acid formed was distilled off at 30°C under reduced pressure. The brownish-yellow residue was extracted with boiling petroleum ether, and the extract was condensed to crystallize vinyl methyl terephthalate. Crude

vinyl methyl terephthalate was purified by vacuum sublimation at 80°–100°C, and 25 g of pure vinyl methyl terephthalate was obtained, mp 61.0–61.5°C (found: C, 63.87%; H, 4.83%).

Poly(vinyl methyl terephthalate) was prepared by radical polymerization. To 3.1 g of vinyl methyl terephthalate, a solution of 0.021 g of azobisisobutyronitrile in 3 ml of benzene was added, then the mixture was heated at 60°C in a glass ampoule. After 21 hr, the reaction mixture was coagulated in petroleum ether, and the polymer was collected.

The intrinsic viscosity and Huggins' viscosity parameter k' were measured by an Ubbelohde viscometer in *o*-chlorophenol at 25°C.

Acid value was determined by titration according to Pohl's method.¹⁴

Infrared absorption spectra were obtained by KBr disk or NaCl plate techniques using a Hitachi EPI-S2 infrared spectrophotometer.

The gas-liquid chromatographic retention data were obtained on a Yanagimoto Model G8 temperature-programmed, dual-column gas chromatograph with thermal conductivity detection. Two 4 mm × 1.5 m stainless steel columns packed with 10% polyethylene glycol, 20M, on 40–60 mesh acid-washed and silanized Celite 560 were used.

Thin-layer chromatographic analysis was carried out as follows: An aliquot of sample solution was spotted onto a Kiesel Gel F 254 plate (Merck, layer thickness 0.25 mm), dried for solvent, and developed with *n*-butanol–methyl ethyl ketone (50:50) or chloroform, and the chromatograms were visualized by means of a bromocresol purple indicator.

Terephthalaldehydic acid in the sublimate was determined by polarography. Into an ammonia–ammonium chloride supporting electrolyte solution, 1.5 g of sample was dissolved, and the insoluble part was filtered off. To the filtrate was added 0.25 ml of 0.5% gelatin solution, and the supporting electrolyte solution was added to adjust the total volume to 25 ml. Current–voltage curve was taken on a Yanagimoto PA-102 polarograph, and from the wave height of the second reduction wave at –1.10 V, the terephthalaldehydic acid content was determined.

The thermogravimetric curve and the DSC curve were taken on a Shimadzu thermobalance TM-2 and a Perkin-Elmer DSC-1B, respectively.

References

1. L. H. Buxbaum, *Angew. Chem., Int. Ed.*, **7**, 182 (1968).
2. H. Sobue and J. Kajiura, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **62**, 1766 (1959).
3. S. Hoffrichter, *Faserforsch. Textiltech.*, **19**, 304 (1968).
4. A. Charlesby and S. H. Pinner, *Proc. Roy. Soc., Ser. A*, **249**, 367 (1959).
5. A. Mifune, S. Ishida, A. Kobayashi, and S. Sakajiri, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 992 (1962).
6. H. Zimmermann and E. Leibnitz, *Faserforsch. Textiltech.*, **16**, 282 (1965).
7. H. Zimmermann, *Faserforsch. Textiltech.*, **17**, 228 (1966).
8. I. E. Kardash, A. N. Pravednikov, and S. S. Medvedev, *Dokl. Akad. Nauk SSSR*, **156**, 658 (1964).
9. T. Ozawa, M. Kanasashi, R. Sakamoto, and M. Ohama, *Preprints for the 18th Conference on Polymer, Japan*, 321 (1969).

10. L. H. Buxbaum, *ACS Polymer Preprints*, **8**, 552 (1967).
11. N. V. Mikhailov, L. G. Tokareva, K. K. Buravchenko, G. M. Terekhova, and P. A. Kirpichinkov, *Vysokomol. Soedin.*, **4**, 1186 (1962).
12. E. P. Goodings, *Soc. Chem. Ind. (London) Monograph No. 13*, 211 (1961).
13. F. B. Marcotte, D. Campbell, J. A. Cleaveland, and D. T. Turner, *J. Polym. Sci. A-1*, **5**, 481 (1967).
14. H. A. Pohl, *Anal. Chem.*, **26**, 1614 (1954).

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