The Viscometric Properties of Polyesters. I. A Comparison between Crystalline and Amorphous Polyesters

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(Received May 23, 1963)

The need for knowledge of the factors influencing the viscometric property of linear polyesters and for an interpretation based on the molecular theories of these relationships has increased with the technological advances of recent years. In order to gain a satisfactory understanding of flow, detailed data are required on well-defined polymers, linear polyesters for example, over a wide range of temperature.

Fox et al.[1] have reviewed recent research on the viscosity of polymers and their concentrated solutions. In their review the experimental problems, the data actually measured and the empirical laws of flow are discussed, and besides, the results are interpreted in terms of qualitative quantitative molecular theories of flow.

The purposes of this experiment are, (1) to deduce the relationship between the chemical structure and the viscometric property of long chain polyesters, (2) to gain detailed information about viscosity over a wide range of temperature, and (3) to point out several interesting problems incident to these results.

1) T. G. Fox, S. Gratch and S. Loshaek, "Rheology," Vol. I, Academic Press, New York (1956), Chap. 12.

For polyester, Flory[2] has already measured their viscosity extensively and has quantitatively examined the influence of molecular weight and temperature on viscosity.

Takayanagi et al.[3] have also studied the temperature dependence of viscosity over a wide range of temperature and applied Bueche's[4] theory to their results. The present author has suggested in a previous report[5] that, for the study of the viscometric property of polyeters, it might be necessary to compare the crystalline with the amorphous polyesters in connection with the viscometric property in the super-cooled liquid state of low molecular substance.[7] Moreover, for the purpose of confirming this opinion, the viscosity of aliphatic polyesters with similar simple chemical structures has been studied in detail. However, discussions of the viscosity of polyesters should be based on exact and detailed experimental results for many kinds of polyesters over a wide range of viscometric conditions; therefore, the present experiment may be considered only an attempt in this direction.

Experimental

The Measurement of Viscosity.—Generally it is important to select a suitable instrument for rheological studies. The rotational viscometer is more useful than the capillary one to obtain the temperature dependence of a steady flow viscosity over a wide range of temperature. The former can easily measure viscosity in several seconds at any desired temperature; therefore, there is little need of a fine temperature regulator if the temperature of the apparatus is observed closely.

Under normal conditions of measurement, for the purposes of this experiment, we may regard the linear long chain polyesters with relatively low molecular weights (about 2000) as almost Newtonian fluids.[5]

The viscometer used in this experiment was as follows:

Rotational viscometer (Brookfield type)
Measuring range: $10^{-1}\sim10^{3}$ poises
Shear rate: 6~60 r.p.m. (4-stage change)

The Preparation of the Polyesters.—Aliphatic long chain polyesters with a low viscosity were prepared by the ordinary method. The combinations of acid and glycol are shown in Table I.

The polyesters were prepared in a 2-liter, 4-necked flask equipped with a thermometer, an inlet tube for inert gas, a device for the azeotropic removal of water, and a mechanically-sealed agitator. In most cases 3 mol. of acid and 3.3 mol. of glycol were reacted under a xylene reflux until the acid number was reduced to approximately 50; this was accomplished by the continuous agitation arising from the introduction of a stream of inert gas. Next, such residual volatile matters as water, glycol and acid were removed by vacuum distillation until the acid number was reduced to approximately 30.

Measurement of the Melting Point of the Crystalline Polyester.—In the polyesters used in this experiment, we can easily distinguish the crystalline from the amorphous one. A certain group of polyesters changes abruptly from the transparent liquid state to the opaque solid state at a certain temperature if they are cooled slowly in the melted state. As a result of the solidification, no viscosity under this temperature can be obtained. On the contrary, there is an other group of polyesters which cannot solidify or for whom it is extremely difficult to solidify from the melted state, even when kept at a low temperature near the glass transition point for several days.

In this report the former and the latter groups of polyesters are termed the crystalline and the amorphous respectively. If the temperature dependence of the infrared spectrum of polyester is studied, the crystalline band is observed for the crystalline, but not for the amorphous.[8]

The melting point of the crystalline was measured with a polarizing microscope. Usually the value of the melting point of any crystalline polymer is somewhat different from its solidifying point which can be pointed out in measuring its viscosity.

Results and Discussion

As the full curve of viscosity can be obtained easily over a wide range of viscosity (about $10^{-1}\sim10^{6}$ poises) in the case of amorphous long chain polyesters of a low viscosity, it seems that these kinds of polyesters may serve as typical models for rheological studies.

The aliphatic saturated polyesters used in this experiment are listed in Table I.

The temperature dependence of the steady flow viscosity in the range of $10^{-1}\sim10^{3}$ poises is shown in Figs. 1—2 for amorphous polyesters and in Fig. 3 for crystalline polyesters.

Within the limits of these aliphatic long chain polyesters, the viscosity-versus-temperature curves are very similar to one another; the very small difference in viscosity may depend on the change in chemical structure.

Since all samples were prepared to have similar molecular weights (1600~2000), the results of this experiment are not considered to have been remarkably affected by the differences in molecular weights of the samples.

2) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1057 (1940).
3) M. Takayanagi and S. Kuriyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kōgyō Kagaku Zassi*), **59**, 49 (1956).
4) F. Bueche, *J. Chem. Phys.*, **21**, 1850 (1953).
5) R. Nakatsuka, Y. Yoshida, *Kagaku to Kogyo* (*Osaka*), **30**, 82 (1956).
6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press (1953), p. 49.
7) C. Dodd and Hu Pak Mi, *Proc. Phys. Soc.*, **B 62**, 454 (1949); N. N. Greenwood and R. L. Martin, ibid., **A 215**, 46 (1952).
8) Presented at the 12th Annual Meeting of Thermosetting Resins, Osaka, October, 1962.

TABLE I. MELTING POINT OF SOLID-STATE POLYESTER (°C)

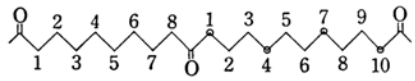
Type	Glycol		Acid			
			Su (2)	Ad (4)	Az (7)	Se (8)
Ordinary type	Et	(4)	—	—	—	69
	Pr	(5)	—	—	36	49
	i-Bu	(5′)	—	a	a	a
	n-Bu	(6)	34	45	39	53
	Pe	(7)	—	—	41	51
Ether type	DE	(7)	a	a	0	33
	DP	(7′)	a	a	a	a
	TE	(10)	a	a	a	29

Note

	Conventional	IUPAC
(1) Su :	Succinic Acid	Butanedioic acid
Ad :	Adipic acid	Hexanedioic acid
Az :	Azelaic acid	Nonanedioic acid
Se :	Sebacic acid	Decanedioic acid
Et :	Ethylene glycol	1,2 Ethanediol
Pr :	—	1,3 Propanediol
i-Bu :	—	1,3 Butanediol
n-Bu :	—	1,4 Butanediol
Pe :	—	1,5 Pentanediol
DE :	Diethylene glycol	2,2′-Dihydroxydiethyl ether
DP :	Dipropylene glycol	2,2′-Dihydroxydipropyl ether
TE :	Triethylene glycol	1,2-Ethanediol bis(2-hydroxy-ethyl ether)

(2) a : Amorphous c : Crystalline

(3) Figures listed in brackets indicate the numbers of members in the main chain belonging to an acid or glycol component of the linear polyester, and a figure with a prime corresponds to a linear polyester with side chains.
For example :



Se (8) TE (10)
Triethylene sebacate (8—10 polyester)

TABLE II. CENTER OF THE "TRANSITION AREA" FOR VISCOUS FLOW (°C)

Type	Glycol		Acid			
			Su (2)	Ad (4)	Az (7)	Se (8)
Ordinary type	Et	(4)	—	—	—	c
	Pr	(5)	—	—	c	c
	i-Bu	(5′)	79	72	45	32
	n-Bu	(6)	c	c	60	c
	Pe	(7)	—	—	c	c
Ether type	DE	(7)	80	51	53	c
	DP	(7′)	75	46	27	34
	TE	(10)	71	52	34	c

A Comparison between the Crystalline and the Amorphous Polyesters.—Aliphatic linear polyesters without side chains are generally crystalline, with the exception of diethylene adipate and several polymers similar to it.[6] As Table I shows, what are called "ether-type polyesters" with ether bonds in the main chain, prepared from such polyglycols as diethylene or triethylene glycol, show a peculiar behavior in their crystallizing tendency.

Though such "ether-type polyesters" without side chains[6] as diethylene adipate are generally recognized to be amorphous, several crystalline "ether-type polyesters" were found among the samples prepared and used in this experiment. Accordingly, we can easily select several sets of polymers very similar in chemical structure, while differing in crystallinity, and compare their viscosities. For example, triethylene azelate is amorphous and triethylene sebacate is crystalline, while both are very similar in chemical structure and viscometric

property over the range of temperature higher than their melting points.

In other words, as is apparent from Figs. 1 and 2, the difference in viscosities between sebacate and azelate in combination with various glycols is so little as to be almost negligible, independently of whether they are crystalline or amorphous.

The relation between chemical structure and crystallizing tendency is shown in Table I.

It seems well established by Table I (1) that every polyester with side chains which was prepared from 1,3-butanediol or dipropyleneglycol is amorphous; (2) that all the ordinary aliphatic-saturated polyesters without side chains or ether bonds in the main chains are crystalline, and (3) that "ether-type polyesters" without side chains are not always crystalline. For example, triethylene azelate and triethylene sebacate are similar in chemical structure, but the former is amorphous and the latter crystalline. Yet both show a very similar viscosity vs. temperature behavior within a comparatively wide temperature range, including the melting point of the latter.

The difference in the crystallizing tendencies of polyesters is probably caused by the intramolecular rotation of the ether bond being easier than that of the methylene bond. From Table I, it may be found that the crystallizing tendencies are relative to the ratio, (m/n), of the number of methylene members of the acid component, (m), to the number of oxygen plus methylene members of the glycol component, (n), in the "ether-type polyesters." That is, "ether-type polyesters" may be shown as follows:

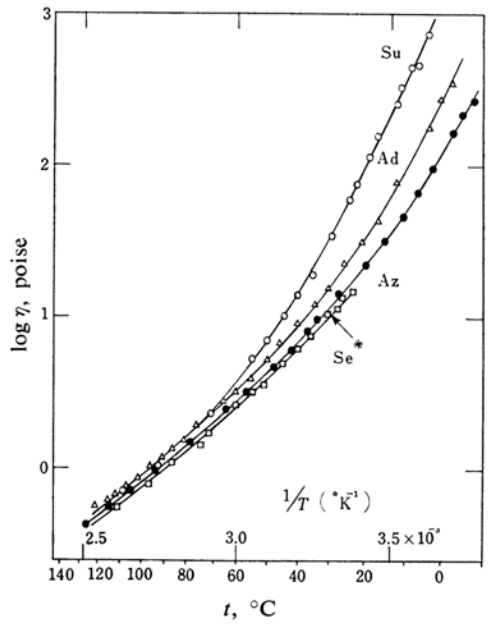


Fig. 1. Relationship between viscosity and temperature (triethylene glycol series).

* Crystalline polyester
↓ Melting point

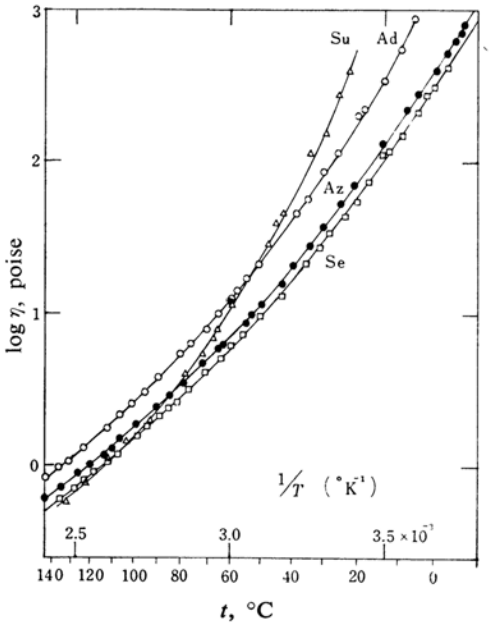


Fig. 2. Relationship between viscosity and temperature (1,3 butanediol series).

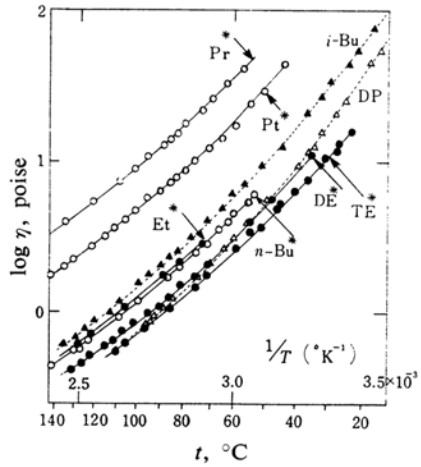
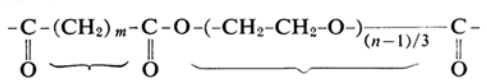


Fig. 3. Relationship between viscosity and temperature (sebacic acid series).

* Crystalline polyester
↑ Melting point



The corresponding numbers for various acid or glycol components are shown in Table I.

For example, in crystalline diethylene sebacate, the numbers of chain members of the acid and the glycol components are 8 and 7 respectively. On the contrary, in amorphous diethylene adipate, the numbers are 4 and 7 respectively. It can be said that "ether-type polyesters" in which m/n is approximately equal to 1 are crystalline.

In order to study their crystallizing tendency further, some polyesters were prepared from such a higher aliphatic dibasic acid as brassylic acid. Both diethylene brassylate (11—7 polyester) and triethylene brassylate (11—10 polyester) were crystalline, as was to be expected.

However, the author believes that further investigation into this matter is required in order to conclude that the ratio of the numbers of members between the methylene of the acid and the ether chain of the glycol is very significant in the crystallizing tendency of "ether-type polyesters."

The $\log \eta$ vs. $1/T$ curves are shown in Figs. 1 and 2 for the amorphous and in Fig. 3 for the crystalline. The slopes of these curves are proportional to the apparent activation energy (E^*) for viscous flow in the Andrade equation:

$$\ln \eta = \ln A + E^*/RT$$

where A and E^* are constants, and R is the gas constant.

Generally, over a wide range of temperature, no apparent activation energy (E^*) of any polyester is constant, no can the curve of $\log \eta$ against $1/T$ be regarded as a straight line.

The findings on the connection between the viscometric property and the crystallizing tendency are as follows:

As Figs. 1—3 show, in the range of temperature higher than the point corresponding to their melting points, all $\log \eta - 1/T$ curves of polyesters used in this experiment are nearly parallel to one other, in spite of their differences in crystallinity and their differences in chemical structure.

Therefore, in a perfectly molten state, or in a state wherein molecules can flow practically free of molecular interaction, the E^* values of the polyesters practically coincide and tend to approach a fixed value when the temperature is raised.

Moreover, when polyesters with similar chemical structures, such as several pairs of sebacate and azelate combined with the same glycol, are compared, it may be seen that almost all the $\log \eta - 1/T$ curves overlap over a wide range of temperature when they are shifted along the η-axis.

On the contrary, in the range of temperature lower than the point corresponding to the melting point of the crystalline counterpart, the discrepancy in the temperature dependence of the viscosity of amorphous polyesters may be ascribed to the differences in their chemical structures.

By comparing the temperature dependence of the viscosity of the crystalline polyesters with that of the amorphous ones, it may be seen that the mechanism of the viscous flow of the latter changes discontinuously in a certain temperature region near the melting point of the corresponding crystalline polyesters. In other words, it seems that in the range of temperature lower than the melting point of crystalline polyesters, a certain sort of force acting on molecules of the crystalline polyesters also exists in the case of the corresponding amorphous polyesters and that this is a cause of the change in their viscous flow state.

"Transition Area" near the Melting Point.— As has been stated above, it has been inferred that there exists a "transition area" for viscous flow in amorphous polyesters in the region of temperature near the melting point of crystalline polyesters with similar chemical structures.

When the temperature is raised beyond the "transition area," the viscous flow of every polyester aproaches an "Andrade liquid state." Though the absolute values of the viscosity of all polyesters are not always equal, their apparent activation energies at a fixed temperature become almost equal. That is, if the difference in molecular weight between polyesters is negligible, the A constant in the Andrade equation depends upon the chemical structure, but the E^* constant does not. With temperature change within the "transition area," the viscous flow state of each polyester begins to change remarkably according to its chemical structure. When the temperature is lowered near the glass transition temperature of each polyester, the $\log \eta - T$ curves, independently of the chemical structure of each, become parallel with one another.

It is clear that the effect of chemical structure on viscosity becomes most remarkable near the "transition area." For example, as Fig. 1 shows, in the case of the triethylene glycol series, the longer the chain of the acid component, the smaller the value of the apparent activation energy.

This relation can be more directly represented by plotting the curves of $\log \eta - 1/T^2$ in Figs. 4 and 5. The curve for each polyester is virtually represented by two intersecting straight lines.

This point of intersection may be regarded as a center of the "transition area" of each amorphous polyester; in the case of crystalline polyesters, with the exception of diethylene

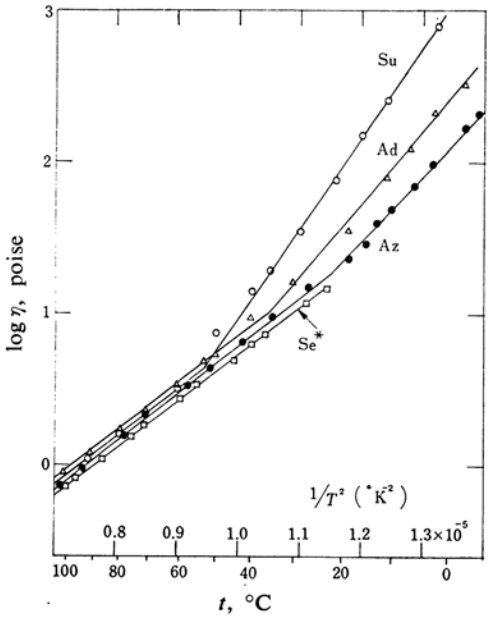


Fig. 4. Relationship between viscosity and temperature (triethylene glycol series).

* Crystalline polyester
↓ Melting point

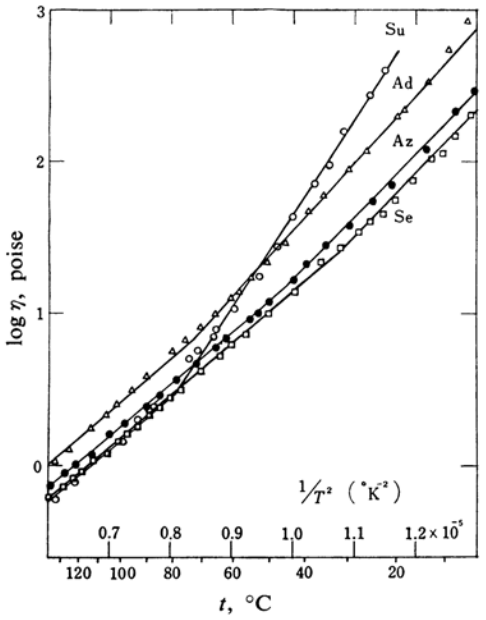


Fig. 5. Relationship between viscosity and temperature (1,3 butandicl series).

azelate whose rate of crystallization is very slow, this point is near the melting point. Therefore, it can be considered that practically no viscosity curve exists beyond this point. As to the relation between $\log\eta$ and $1/T$, all straight lines under this point are almost parallel with one another, irrespective of chemical structure. The values of the "center of transition area" determined by this method are shown in Table II.

By comparing Table I with Table II, it may clearly be seen that the center of the "transition area" of an amorphous polyester almost corresponds to the melting point of a crystalline polyester. This experimental fact shows the close connection between the "transition area" and the melting point.

The Temperature Dependence of the Activation Energy for the Viscous Flow near the "Transition Area".—The relationship between E^{*} and $1/T$ over the range of viscosity 10^{-1} $\sim10^{3}$ poises is shown in Figs. 6 and 7. For example, as Fig. 6 shows, these relations are represented as nearly S-type curves, and the center of the "transition area" is regarded as being practically the point at which the slope of the $E^{*}-1/T$ curve is steepest. The values of the viscosity and apparent activation energy at this point reach about 10 poises and about 11 kcal./mol. respectively.

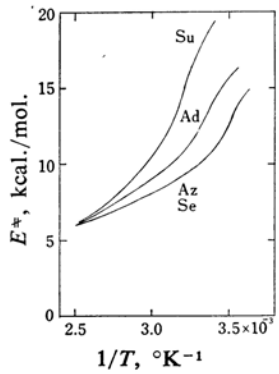


Fig. 6. Apparent activation energy for viscous flow (triethylene glycol series).

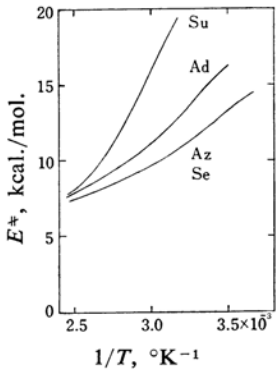


Fig. 7. Apparent activation energy for viscous flow (1,3 butanediol series).

The $E^{*}-1/T$ curve in the range of high viscosity ($10^{3}\sim10^{6}$ poises) will be shown in a the next report of the present series.

As has been stated above, by studying the relations between $\log\eta$ and $1/T$, $\log\eta$ and $1/T^2$, and E^* and $1/T$, it may be easily deduced that there is a "transition area" for the viscous flow in the case of aliphatic long-chain polyesters. However, this concept is quite different from that regarding the glass transition point discussed previously, because the abrupt changes of temperature dependence in the infrared absorption[8] and in the refractive index are not observed in the transition area." In the "transition area" for the viscous flow, the viscous flow mechanism changes suddenly and, accordingly, it should be possible to distinguish viscometric properties between the higher and the lower temperature.

However, at present, it can be said with certainty only that no abrupt change in the arrangement of long chain molecules as shown at the crystallizing point has yet occurred at this stage.

In this manner, the existence of the "transition area" is more clearly shown in the relationship between E^* and $1/T$ than in the $\log\eta - 1/T$ curves.

Every apparent activation energy (E^*) at a certain temperature within the "transition area" differs from the others according to the chemical structure of each polyester, and the abrupt rise of E^* in the same area shows the change of interaction among linear polyester molecules with many dipoles.

The effects of chemical structure on E^* may be compared approximately as follows:

Glycol series

dipropylene glycol $>$ diethylene glycol $>$ triethylene glycol $\fallingdotseq$ 1,3-butanediol

Acid series

succinic acid $\gg$ adipic acid $>$ azelaic acid $\gg$ sebacic acid

It seems usual that the larger the chain between two adjacent carbonyl groups in a homologous series of polyesters, the lower the apparent activation energy near the "transition area." This phenomenon may be caused by the diluting effect of larger chains for dipole interaction.

However, it seems unusual that both triethylene glycol and 1,3-butanediol have the effect of reducing E^*, in spite of the fact that the side chains of 1,3-butanediol generally increase the E^* value because of their effect of reducing the fluxibility of long-chain molecules.

From these experimental results, it may be presumed that the methylene chain is more flexible than the ether chain in the "transition area" for viscous flow, and that the ether bond has a smaller dependence of intramolecular rotation on the temperature than does the methylene bond.

Summary

From the study of the viscosity of aliphatic long-chain polyesters over a wide range of temperatures, the following results have been obtained:

(1) Among aliphatic long-chain polyesters with ether bonds in the main chains, several crystalline polyesters have been obtained.

(2) Accordingly, it has been possible to compare the temperature dependence of the viscosity of the amorphous and the crystalline polyesters with similar chemical structures.

(3) When the temperature is raised, every apparent activation energy for viscous flow (E^*) approaches a fixed value, independently of the chemical structure of the polyester.

(4) However, the viscous flow state of the amorphous polyester changes discontinuously in connection with the chemical structure near the melting point of the corresponding crystalline polyester.

(5) In the "transition area" for viscous flow, the viscosity and the apparent activation energy (E^*) are, respectively, about 10 poises and 11 kcal./mol.

The author is indebted to Professor Hiromu Murata of the Faculty of Science, Hiroshima University for his helpful discussions and encouragement throughout the work, and to Dr. Keiji Oshima, Director of the Osaka Municipal Technical Institute for his advice and encouragement. He also wishes to express his gratitude to Mr. Tadao Nakao, Senior Managing Director of the Sumitomo Bakelite Co., Ltd., and Director of the Central Research Laboratory of the same company, for permission to publish this paper, and to Mr. Kyosuke Miki and Mr. Shozo Yoshizumi of this Laboratory for their valuable assitstance.

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Sumitomo Bakelite Co., Ltd.
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