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Flow Properties of Copolymer Solutions.
Measurements with a Cone-and-Plate
Viscometer

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A cone-and-plate viscometer is constructed, which is suitable for measurements of viscosities from 1.0×10^{-1} to 1.0×10^{7} poises at rates of shear of 3.60×10^{-2} to 1.41×10^{2} sec^{-1}.

Some results are given of measurements on solutions of three different types of copolymer, *i.e.* the block, the alternating, and the random copolymers, of methyl methacrylate (MMA) and styrene (S) with nearly equimolar composition. In chlorinated biphenyl, a good solvent for the both components, all the solutions exhibited the non-Newtonian flow behavior. The shear rate-temperature superposition was achieved for viscosity data of solutions of the alternating and the random copolymers but not for the solution of triblock copolymer consisted of linear chains of PMMA-PS-PMMA. In a mixture of diethyl phthalate and dioctyl phthalate, in 3 : 7 mole ratio, the viscosity of the solution depended on shear history as well as shear rate.

INTRODUCTION

It is now well established that the variation of sequence distribution of components along a copolymer chain affects strongly upon the physical properties of solid samples.[1~3] For instance, random copolymer, in which two components are uniformly distributed along the polymer chain, exhibits a single glass transition temperature and a very narrow peak of dynamic loss corresponding to the transition.[2a] This shows that no segregation of components of the copolymer occurs and that each component is distributed uniformly throughout the system, even when two components are mutually incompatible. On the other hand, block copolymers consisting of two amorphous components shows two glass transitions which are assigned to those of the homopolymer components.[1] This behavior is attributed to their two-phase domain structures due to segregation of each block. Many recent works have been devoted to clarify how are modified the domain structures by the variation of factors such as composition of components and nature of solvent from which solid samples are cast. Various types of domain structure are actually observed by electron microscope.

Heterophase structures are also manifested in systems of block copolymer and solvent in their liquid state. Extensive studies, both theoretical and experimental, concerning the microphase separation in block copolymer solutions have been reviewed recently by Sadron and Gallot.[4] General phase diagram of diblock copolymer and solvent system has been given in the review, and the existence of aggregates and that of domain structures has been suggested in the moderate and the high concentration regions, respectively. Thus for the moderately concentrated, or concentrated, solutions of block copolymer,

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it may be expected that large aggregates, or network, of block copolymer molecules will be developed in the solution and that the solution shows flow properties different from those of random copolymers. Furthermore, complicated dependence of flow properties on shear rate and shear history might be observed under some testing condition. However, to the authors' knowledge, little has been done on flow properties of concentrated solutions of block copolymer.[5]

In order to study flow properties of copolymer solution, especially of block copolymer solution, by varying concentration, temperature, and rate of shear, we built a cone-and-plate viscometer. This paper presents the design and the method of measurements of the viscometer. The results of some preliminary measurements are also given, which were made on solutions of copolymers of methyl methacrylate and styrene, with different architecture, in chlorinated biphenyl and a mixture of diethyl phthalate and dioctyl phthalate. Flow behavior of the block copolymer solutions studied in a variety of conditions of experiment will be reported in a forthcoming article, by placing emphasis upon the dependence of viscosity on shear rate and shear history.

DESCRIPTION OF THE APPARATUS

The rotational viscometer which has been constructed at our laboratory is of the cone-and-plate type. We have made this choice by the following reason. As described above the existence of domain structures due to the microphase separation of components of the A-B-A type or the A-B type block copolymer systems is anticipated even in a solvent being good for the both components except for very low concentration region. In a certain region of concentration the structures might be easily modified by a little variation of the shear rate; in other words, it might be expected that the non-Newtonian behavior may be readily observed for the system concerned. If viscosity measurements of solutions of the block copolymer are made by using the coaxial-cylinder type apparatus, for instance, the shear rate is not uniform across the gap, and this might need some complex manipulations in estimating the effect of the shear rate on viscosity because rather wide gap should be used in the case. Such unfavorable situation may be avoided by the use of the cone-and-plate type apparatus since, if the gap angle does not exceed a few degrees, the shear rate is virtually constant throughout the gap.

Figure 1 gives a schematic representation of the viscometer. The torsion head TH with a torsion wire TW, a torsion shaft TS, and the upper platen, i.e. the cone, UP is firmly supported on top of a thick column C. The lower end of TS is shaped into a thin rod with a conical pivot and is sticked out a little through UP. The column and a lower bearing housing LB are tightly attached to a heavy steel base B of the apparatus. The column also carries a sample chamber SC and a stay ST with an upper bearing housing UB. The former closes around the measuring faces, cone-and-plate, and is supplied with heat-exchange fluid from a heating or a cooling system.

A specimen S is held in the gap between UP and the lower platen LP on which a thin hole and a circular groove is hollowed at the center and close to the edge, respectively. The thin hole, together with the pivot of TS mentioned above, will help to align the axes of TS and LP. When LP is rotated, a force exerted on UP is measured by the twist of TW. A linear variable differential transformer detects the twist by measuring the
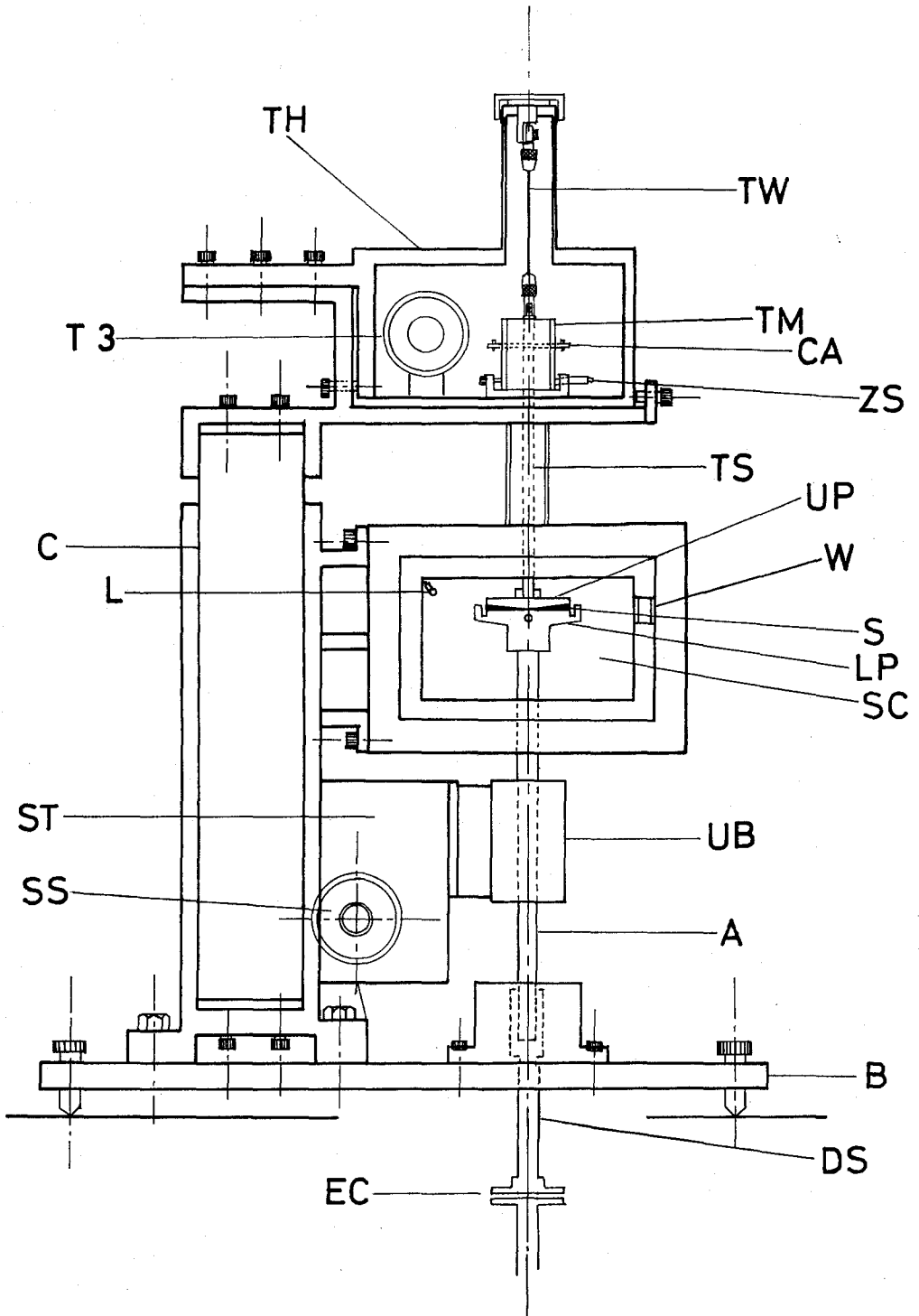
Fig. 1. Schematic diagram of the cone-and-plate viscometer. Base B of the viscometer with column
C and torsion head TH. Rotating member: Electromagnetic clutch EC, driving shaft DS, axle
A, and lower platen LP; A is connected with DS by the key and slot in lower bearing housing
LB. Torsion head TH with torsion wire TW, torsion shaft TS, and upper platen UP. Trans-

former mounted on transformer mount TM measures the deflection of cross arm CA. Zero positioning of angle detecting system is made by zero positioning set screw ZS, and heating effect on detecting system is eliminated by transformer T3. Stay ST with upper bearing housing UB is driven by stay set screw SS. SS is used for clearance setting after filling with specimen S between platens. Sample chamber SC bears window W in the front and small lamp L inside.

displacement of iron cores which are placed on both ends of cross arm CA. The signal from the transformer is recorded on a moving strip chart via a millivolt converter. The range of twisted angles from 1×10^{-3} to 2 degrees is measurable with high precision. Torsion wires of the same length having diameters from 0.6 to 4.0 mm are used in the study. The wires are precalibrated by the free damped oscillation method with pendulums of known moment of inertia. Six wires cover the range of torsional coefficient from 4.323 $\times 10^2$ to 3.628×10^6 dyne-cm/deg.

The lower platen is locked on the top of an axle A, and in LB the latter is connected by the key and slot to a spigoted end of a driving shaft DS. Power is derived from a 1/4-h.p. moter, which runs at speeds from 4 to 40 r.p.m. by means of a combination of variable-speed device (ring-and-cone) and a geared speed reducer, and is transmitted to DS through a transmission. The latter consists of gear train and a friction gearing, and is fitted with a handle that can vary the speed of output shaft continously over range of reduction ratios from 1 : 1 to 200 : 1. Also an electromagnetic clutch EC is provided between DS and the output shaft of the transmission and enables immediate and sharp starts and stops.

The rotational speed of DS is measured by a tachometer, which is precalibrated by measuring the time required for a hundred rotations of the lower platen. Constant number of rotation of DS to less than 0.1% is maintained over the available range of rotations.

Five interchangeable pairs of platens are provided for measurements. The cone angle ϕ of the upper platen has been determined by the lamp and scale method: *i.e.* a mirror is fixed near the axis of the cone, and the light beam from a source of light is reflected back on the vertical scale. The cone is then inclined an angle 2ϕ, and the corresponding traveling distance h of the image is read on the vertical scale. If the distance l between the axis of the cone and the lamp and scale is sufficiently long compared with h, ϕ can be calculated by the following equation:

$$\phi = \frac{h}{4l} \tag{1}.$$

The values of ϕ of the cones has been determined with the precision of $\pm$ 1 minute, and are listed in Table I. Thus the apparatus will measure viscosities in the range of $1.0 \times$

Table I The Values of Radius R and Cone Angle ϕ for Five Platens

No.	R, cm	ϕ, deg.
1	1.50	3.33
2	2.00	1.74
3	2.00	2.87
4	3.00	1.70
5	3.00	2.87

10^{-1} to 1.0×10^7 poises at rates of shear of 3.60×10^{-2} to 1.41×10^2 sec^{-1} with combinations of pairs of platens and torsion wires (Equations (2) and (3) given below).

TEMPERATURE CONTOROL

The platens are enclosed by the hinged chamber with jacket through which is circulated a heat-exchange fluid. The outer wall of the chamber SC is covered with asbestos. In order to observe the free surface of the sample in the gap during the measurement SC bears a window W in the front and a small lamp L inside. In the region of temperature from 5° to 70° rapid change of temperature and adequate control of the sample temperature is facilitated by the circulation of the heat-exchange fluid, *i.e.* water or oil.

At temperatures higher than 80°, however, the heat flow along the axle A does not compensate the heat supply from the heat-exchange fluid circulated in the jacket. To obtain an improved control of sample temperature in this region an auxiliary heater surrounded A is operated by the use of a slide-type adjustable autotransformer. With the device fast attainment of thermal equilibrium in SC and satisfactory control of the sample temperature are achieved. In order to prevent unfavorable heating effect on the detecting of twist angle caused by heat flow along TS, the third transformer is placed in TH. The transformer can eliminate the drift of output signal of the detecting transformer system with varying temperature.

The temperature is measured by a copper-constantan thermocouple placed in SC. To investigate a possibility that the temperature measured in this manner differs from that of the sample, in the whole range of temperature studied the latter was determined by a second thermocouple inserted into the hole provided in LP, and no detectable difference was observed. Also no appreciable distribution of temperature was found in SC. Constant temperature to within $\pm$ 0.1° is maintained over a range of temperatures from 5° to 150°.

In cases that a sample is easily cross-linked or degraded by the existence of oxygen, a nitrogen atmosphere may protect the sample from being oxidized. The gas enters SC through a steel tube fitted in one of the halves of the hinged chamber and flows out through a tube fitted in another half.

PROCEDURES AND CALCULATION

A sample, about 0.1–0.2 ml, is placed on the lower platen LP and left standing still until air bubbles have disappeared. The platen is then raised by means of a stay set screw SS up to the position at which the pivot of TS is inserted into the conical hole at the center of LP. Since the axial alignment of TS and LP has been made carefully in advance, the procedure secures that TS and LP will rotate arround the common axis. The lower platen is raised again until it touches the upper cone UP, and is then lowered to keep a certain clearance between the hypothetical apex of the cone and the plate. The touch of the platens may be indicated by the change in output voltage of the twisted angle detecting system.

The increase of the clearance between the platens will cause the decrease of a torque exerted on UP. The relationship between the clearance and the torque has been considered

by Markovitz and others.[6]   It has been found in their apparatus that the best result is obtained not at null clearance between the apex of the cone and the plate but with keeping a certain small value of the clearance.   In our viscometer viscosities of a testing liquid have been measured by keeping the clearance 0.002, 0.003, 0.005 and 0.010 cm.   The values of measured viscosity with clearances 0.002, 0.003 and 0.005 cm were in agreement one another within $\pm$ 0.5%, but was caused lower values in viscosity with 0.010 cm clearance.   In this study the clearance is therefore kept always as 0.002 cm, and this is effected by the use of a dial gauge which moves along with the axle A.

A sample can be held in the gap between the platens by the surface tension and the adhesion to the platens.   After the thermal equilibrium has been attained in SC the indication of the output voltage of the angle detecting system is made null by using a zero positioning set screw ZS.   A known speed of rotation is then given to LP, and the sample is forced to flow under constant rate of shear.   The torsion wire with a known torsional coefficient n is twisted an angle θ and measures the torque.

The viscosity η at a given angular velocity of the plate ω is calculated by the following equation:

$$\eta = \frac{3\,n\phi}{2\pi R^3} \cdot \frac{\theta}{\omega} \tag{2},$$

where R is the radius of the plate.   The rate of shear $\dot{\gamma}$ is simply given by

$$\dot{\gamma} = \frac{\omega}{\phi} \tag{3}.$$

In order to examine the error in viscosity measurements with the apparatus, chlorinated biphenyl and a 30% chlorinated biphenyl solution of a styrene-butadiene-styrene block copolymer were chosen as test liquids, and zero-shear viscosity η_0 were measured at several temperatures.   The values of η_0 measured are compared in Table II with those by the use of a capillary viscometer of the Ubbelohde type for the former and a rotational viscometer of coaxial-cylinder type for the latter.   The agreement is excellent for chlorinated biphenyl, and is also good for the 30% copolymer solution by taking into consideration

Table II.   Comparison of Values of Zero-Shear Viscosity η_0 Measured
with Three Types of Viscometer.

Testing Liquid	Temp., °C	η_0, poise		
		Cone-and-Plate Type	Capillary Type	Coaxial-Cylinder Type
Chlorinated Biphenyl	14.5	1.09×10	1.12×10	—
	30.0	1.30	1.30	—
	39.3	5.46×10^{-1}	5.25×10^{-1}	—
	49.4	2.65×10^{-1}	2.64×10^{-1}	—
30% Chlorinated Biphenyl	19.8	2.43×10^3	—	2.50×10^3
Solution of Styrene-Butadiene-Styrene Block Copolymer	40.5	2.77×10^2	—	3.00×10^2

the fact that an error of several percents is involved in determining η_0 by the coaxial-cylinder viscometer.

EXPERIMENTAL RESULTS

Copolymer samples used in the study are three different types of copolymer of methyl methacrylate (MMA) and styrene (S) with nearly equimolar composition. These samples were furnished through the courtesy of Professors H. Inagaki and T. Kotaka of this Institute. A block copolymer (coded as 62-B-7), which consists of linear chains of PMMA-PS-PMMA, has been prepared by an anionic polymerization technique at $-78°$ with sodium biphenyl in tetrahydrofuran. The triblock copolymer was fractionated by using a large scale column with benzene and n-hexane mixture, and one of the middle fractions was used. The ratio of weight-average to number-average molecular weight M_w/M_n was estimated as about 1.5 from the gel permeation chromatography.

An alternating copolymer (coded as AL-III) has been polymerized at room temperature by a method reported by Hirooka with ethyl alminum sesquichloride and benzoyl peroxide (BPO) in toluene.[7] A random (statistically randomized) copolymer with nearly azeotropic composition (coded as R-50), styrene mole fraction of 0.52, is a low conversion product prepared at 60° by a radical copolymerization method by using BPO as an initiator. These two types of copolymer were not subjected to fractionation, and the whole polymers were studied.

Osmotic-pressure measurements were made by a Mechrolab 503 high speed membrane osmometer. Comonomer composition of the copolymer samples was determined by repeated semimicro combustion analysis. The results are listed in Table III.

Two types of solvent were used to find out how the flow behavior of copolymer solutions will be affected by the difference in solvent nature. Chlorinated biphenyl (Aroclor 1248) and a mixture of diethyl phthalate (DEP) and dioctyl phthalate (DOP), mole ratio of 3 : 7, were used for the purpose. Chlorinated biphenyl and DEP are good solvent of the both components PMMA and PS, and DOP is a solvent for PS but nonsolvent for PMMA.

Testing solutions were prepared by dissolving a copolymer sample in a mixture of a given solvent and dichloromethane (DCM) followed by slow evaporation of the latter. Final traces of DCM were removed by prolonged drying in a vacuum oven at room temperature. The loss of the solvent during the drying process was found to be negligible. The concentration of solutions was calculated from the weights of copolymer and solvent by assuming volume additivity.

Figure 2 gives the logarithmic plots of steady-state viscosity η against shear rate $\dot{\gamma}$

Table III. Copolymer Samples

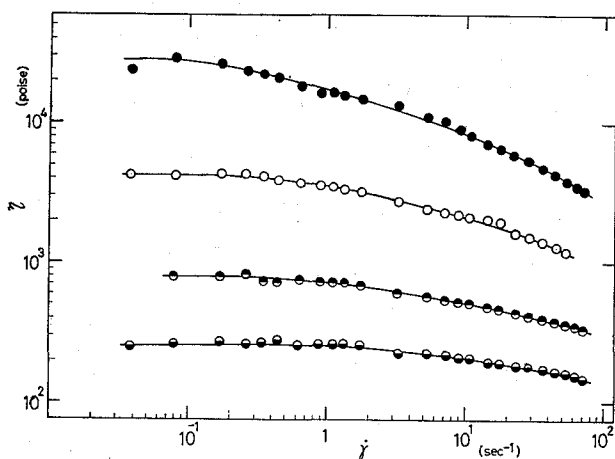| Code	Type	M_n	Mole Percent of Styrene
62-B-7	Triblock	1.44×10^5	52.7
AL-III	Alternating	3.73×10^5	50.0
R-50	Random	2.19×10^5	50.0

Fig. 2.   The logarithmic plots of viscosity against shear rate for the 17.3% solution of the
PMMA-PS-PMMA triblock copolymer 62-B-7 in chlorinated biphenyl.
Temperatures are from the top:
●, 10.2°; ○, 20.0°; ◓, 29.9°; ◑, 36.9°.

at four different temperatures for a 17.3% chlorinated biphenyl solution of the block copolymer 62-B-7.   The similar data for the alternating copolymer AL-III and the random copolymer R-50 in the same solvent are given respectively in Figs. 3 and 4.   The concentration of the former solution is 8.0% and that of the latter is 13.0%.   In all cases studied the non-Newtonian flow behavior is observed in the region of higher rates of shear. The Newtonian flow, on the other hand, is achieved at lower rates of shear, except for data of the solution of AL-III at 9.6°.

Viscosity data shown above suggest a possibility of a shear rate–temperature superposition based on variables

$$\frac{\eta}{\eta_0} \quad \text{and} \quad \dot{\gamma}\frac{\eta_0}{T} \tag{4}$$
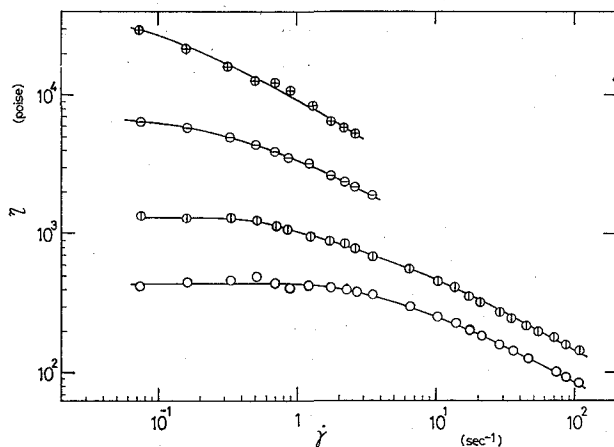
Fig. 3.   The logarithmic plots of viscosity against shear rate for the 8.0% solution of the
alternating copolymer of MMA and S, AL-III, in chlorinated biphenyl.
Temperatures from the top:
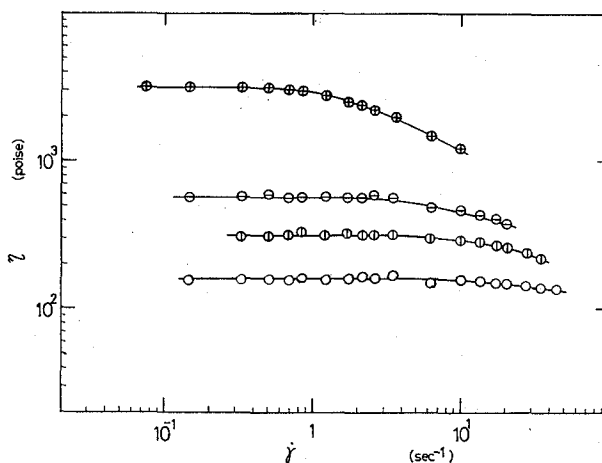⊕, 9.6°; ⊖, 20.7°; ⦶, 31.1°; ○, 40.6°.

Fig. 4. The logarithmic plots of viscosity against shear rate for the 13.0% solution of the random copolymer of MMA and S, R-50, in chlorinated biphenyl.

Temperatures from the top:
⊕, 14.5°; ⊖, 24.5°; ⊕, 29.2°; ○, 37.3°.

where T is temperature of measurements. The reduced plots for the block, the alternating, and the random copolymer solutions are given in Figs. 5, 6(a), and 6(b), respectively. The superposition for the alternating and the random copolymer systems is seen to be good although the range of temperature studied is rather limited. Exactly similar success in the temperature superposition by using reduced variables given in Equation (4) has been demonstrated with concentrated solutions of a typical homopolymer, polystyrene.[8] Also, it is observed in Figs. 6(a) and 6(b) that the limiting slopes of the master curve approach about 1/2 in the region of high reduced rate of shear.

Contrary to the results for the two copolymer systems, the temperature superposition does not quite succeed for the block copolymer solution. Recent studies by Kraus and others on melt flow behavior of copolymers of styrene and butadiene differing in monomer sequence distribution have revealed that the shear rate–temperature superposition is impossible except for uniformly randomized copolymer and that the discrepancies increase with broadening of the composition distribution.[2a,3] The results have been interpreted
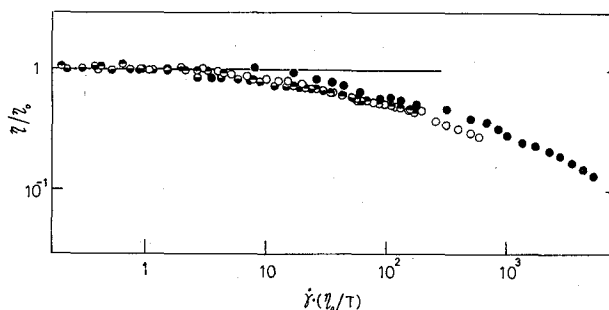

Fig. 5. The reduced plots of viscosity against shear rate for block copolymer 62-B-7 in chlorinated biphenyl. Temperature keys are the same as in Fig. 2.
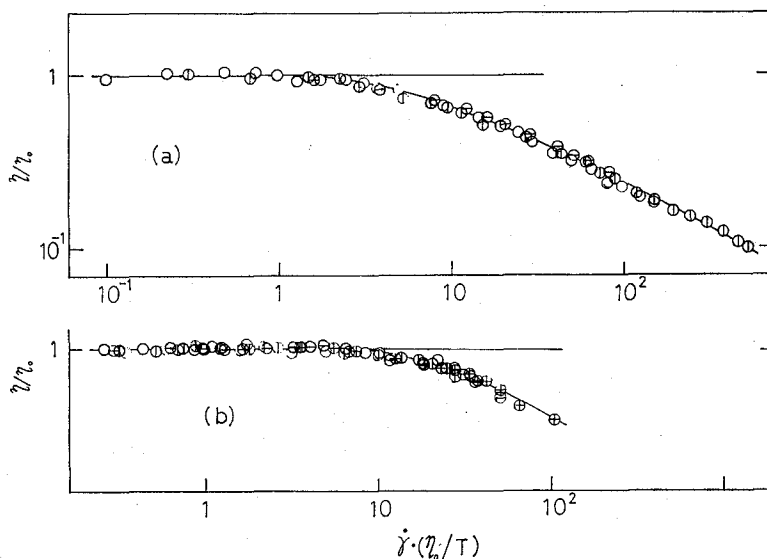
Fig. 6. The reduced plots of viscosity against shear rate.

  (a) The alternating copolymer AL-III in chlorinated biphenyl.
       Temperature keys are the same as in Fig. 3.
  (b) The random copolymer R-50 in chlorinated biphenyl.
       Temperature keys are the same as in Fig. 4.

qualitatively as due to an association of the long sequence of styrene units, to which is attributed a two-phase domain structure similar to that found in the solid state of block copolymers.　A similar association effect of the component MMA may be expected for the solution of the triblock copolymer 62-B-7, and the failure of the temperature reduction might be explained in terms of the existence of aggregates, or network, being formed due to the effect.　For the block copolymer solution the decrease of the reduced viscosities occurs at somewhat lower rates of shear compared with the alternating and the random copolymer systems at nearly the same temperature.　This also might lend support to the formation of large aggregates, probably star-shaped, would be the case in the system even in the concentration region studied.

　　If the domain structure due to the association of MMA sequence is formed in the triblock copolymer solution, it may be anticipated that any effect on flow behavior, which is attributable to the domain structure, will be much more pronounced in a solvent being poorer for PMMA.　In order to clarify how is affected the flow behavior of copolymers by changing solvent from being good to poor for PMMA, viscosity measurements were performed with the system triblock copolymer in the mixture of DEP and DOP.　As described above DOP is a nonsolvent for PMMA, whereas DEP and chlorinated biphenyl are solvents.　Furthermore, if aggregate, or domain structure, developed in the system is easily modified by being subjected to flow it would be possible to observe a history-dependent behavior.　This has been studied at two temperatures by choosing a 17.2% solution of 62-B-7 as a testing solution according to the following scheme: that is, the first measurements of viscosity were made at 30.0° with a virgin sample and the measurements were repeated an hour after the first run by keeping the sample *in situ* at the same tem-
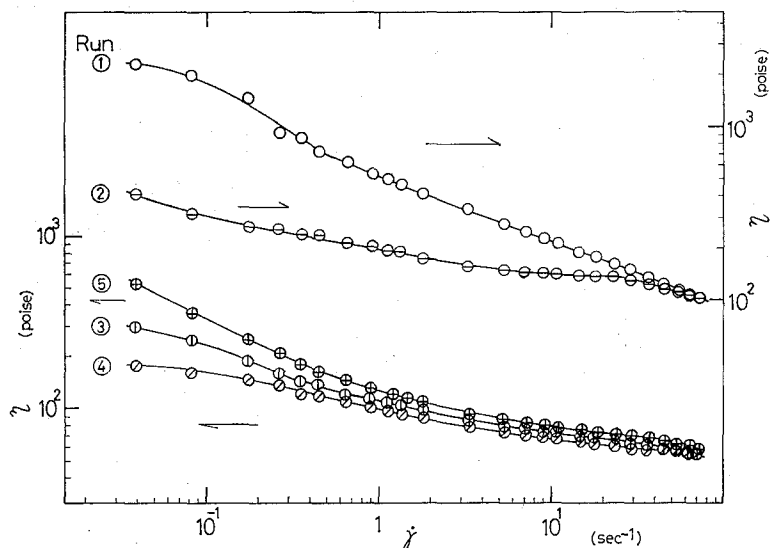
Fig. 7. The logarithmic plots of viscosity against shear rate for the 17.2% solution of the block copolymer 62-B-7 in the mixture of diethyl phthalate and dioctyl phthalate. Run 1 and 2, 30.0°; Run 3 and 4, 40.4°; Run 5, 40.0°.

perature. The temperature was then raised to 40.4° and the third measurements were performed after the attainment of the thermal equilibrium. The measurements at the same temperature were repeated immediately after the third run. After being kept at rest overnight at 40.0°, the sample solution was subjected to the final measurements at 40.0°. Figure 7 gives the results. Viscosity data at different four temperatures for a 17.2% solution of the random copolymer R-50 with the same mixed solvent are shown in Fig. 8 for the sake of comparison. For the latter system a study concerning the history–
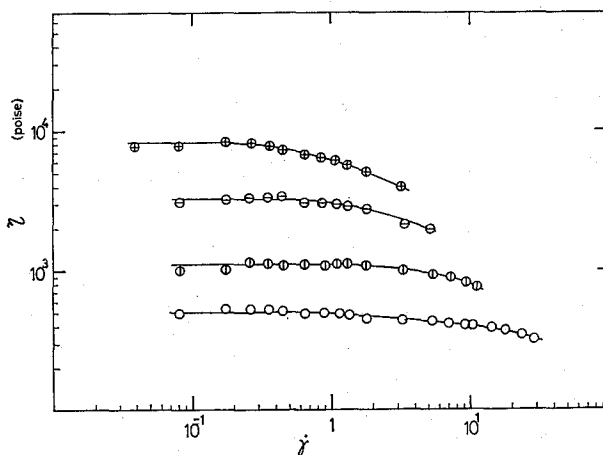

Fig. 8. The logarithmic plots of viscosity against shear rate for the 17.2% solution of the random copolymer R-50 in the mixture of diethyl phthalate and dioctyl phthalate.

Temperatures from the top:
$\oplus$, 13.1°; $\ominus$, 20.7°; $\oslash$, 31.2°; $\bigcirc$, 40.6°.

dependent flow behavior was not carried out because preliminary measurements of viscosity exhibited no history-dependent behavior.

The random copolymer system shows the flow behavior quite similar to that observed with good solvent chlorinated biphenyl. On the other hand, for the triblock copolymer solution the shapes of the η versus $\dot{\gamma}$ curves are different from those observed for the chlorinated biphenyl solution (Fig. 2). The most significant feature observed in Fig. 7 is the strong dependence of measured viscosities on shear history as well as shear rate. The history-dependent nature of flow behavior is more marked at lower temperature and also in the region of lower rates of shear. At the both temperatures the η versus $\dot{\gamma}$ plots having various histories seem to tend to coincide with one another in the region of higher rates of shear. In the curve of the first measurements, run 1, an inflection point is observed at a shear rate of about 5×10^{-1} sec^{-1}. At lower rates of shear the shape of the curve resembles to that observed in the good solvent, and in the region of moderate and high rates of shear plots are approximately represented by a straight line. This may suggest that the solution undergoes a transition in flow properties at the shear rate quoted above. The transition would be closely correlated with disruption of large aggregates being formed at rest, or at very low rates of shear. In this connection, it may be worthwhile to note recent works by Arnold and Meier on dynamic viscosities of styrene-butadiene-styrene block copolymer melts.[9] A marked transition is observed in plots of dynamic viscosity versus deformation rate, and the results have been interpreted in terms of formation of domain of PS and modification of the domain structure with varying rates of deformation.

At 30° the viscosities of the solution of 62-B-7 in the mixed solvent are about twice as high as those in chlorinated biphenyl at rates of shear of about 1×10^{-2} sec^{-1}. However, in the range of higher rates of shear viscosities of the former solution are lower than those of the latter system by a factor of about three. Similar trend is also observed in data of the both systems at 40°. This might suggest that relatively larger aggregates, or more developed network-like structures, formed in the mixed solvent seem to be more easily disintegrated than those formed in chlorinated biphenyl by the applied shear to the system. Also, viscosity data of the triblock copolymer solution at 40° indicate that the large aggregates being disrupted once at higher rates of shear can be reconstructed gradually with the elapse of time at rest.

ACKNOWLEDGMENT

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