JOURNAL OF APPLIED POLYMER SCIENCE VOL. 9, PP. 3177-3193 (1965)

Rheopexy in Some Polar Fluids and in Their Concentrated Solutions in Slightly Polar Solvents

I. STEG and D. KATZ, *Scientific Department, Israel Ministry of Defence, Tel Aviv, Israel*

Synopsis

Several medium and high molecular weight polar fluids, when subjected to shearing forces above a certain rate of shear, showed a rheopectic behavior. The observation was made on some polyesters, an epoxy compound, and on concentrated solutions of these materials in nonpolar solvents. The experiments were carried out in a rotating type viscometer with cone-and-plate arrangements. The following explanation for the observed rheopexy is proposed: above a critical rate of shear, the polar macromolecules after alignment in the field of shear are forming quasicrystallites and a rheological network structure due to intermolecular forces. Because of the simultaneously occurring process of the breaking of structures in the field of shear, a state of pseudoequilibrium is reached. It was found that when the experiments were interrupted at the stage of such a pseudo-equilibrium for a short time, a thixotropic strengthening of the existing structure occurred; under renewed shear the stress decreased to its value before the interruption. After interruption of shear for longer periods (hours, days), a breakdown of the rheopectic structure was observed.

Introduction

According to general rheological considerations, fluids under shear can show Newtonian or non-Newtonian behavior.[1,2] The Newtonian behavior is characterized by a simple linear correlation between the shearing stress τ and rate of shear D during the laminar flow of the fluid. The flow curve is a straight line passing trough the origin of the shearing stress–rate of shear coordinates, and its slope, the viscosity, depends only on temperature and pressure. Non-Newtonian fluids for which the flow curves are nonlinear or have an intercept on the shearing stress coordinate can be divided into two major groups: (*a*) the shearing stress at any point depends only on the rate of shear (at constant temperature and pressure), and after the interruption of shear the stress returns immediately to its initial value; (*b*) the shearing stress versus rate of shear relation depends also on the time the fluid was sheared, on the previous shear history, and the length of the rest period of the fluid between two periods of shear.

The first group, of time independent non-Newtonian fluids, can be subdivided further into three groups: (*1*) Bingham plastics with a flow curve represented by a straight line having a intercept τ_y on the shearing stress coordinate; (*2*) pseudoplastic fluids with flow curves without a yield value and with a progressively falling apparent viscosity η_a. (At high rates of shear, the flow curve becomes linear, and the slope of this part of the curve is defined as the viscosity at infinite shear η_∞. In order to characterize the fluid, the empirical power law proposed by Ostwald[3] and Reiner[4] is used very often.); (*3*) dilatant fluids with flow curves without a yield, and with an apparent viscosity increasing with the rise of rate of shear. Again the power law very often does represent this type of flow, but *n*, the degree of non-Newtonian behavior of the fluid, is greater than unity.

The non-Newtonian time-dependent fluids can be subdivided into two groups: (*1*) thixotropic fluids; (*2*) rheopectic or antithixotropic fluids. In both cases rheological structures are formed due to intermolecular forces and to interaction between the particles of the fluid.

In the thixotropic fluid, the spatial structure forms mostly at rest and is progressively broken down when the material is sheared. The apparent viscosity is decreasing with a rate depending on the rate and duration of shear. With the progressing destruction, or with the increase of the number of available linkages, the structure reforms with an increasing rate, and eventually a dynamic equilibrium, depending on the rate of shear, is reached, and a constant value of apparent viscosity at given conditions is obtained. During rest, the structure builds up again, so that the process is reversible.

Contrary to the previous case, in a rheopectic fluid the structure builds up by shear, and the shearing stress increases with time of shear at a constant rate of shear. At rest the rheopectic structure breaks down. Such time-dependent behavior of fluids is less common than the previous one, but several interesting cases are known.[1b,5,6]

The rheological properties of different fluids, including pseudoplastic linear polymers, determined in a wide range of rates of shear, have been reviewed by Merrill.[7] The pseudoplastic materials were categorized as Ostwald-Philipoff liquids. A detailed study of a typical flow curve of such a liquid shows two Newtonian regions, the first at low rates of shear, the second at high rates of shear, separated by a region of non-Newtonian behavior. In this interconnecting region of "structural flow" the molecules straighten out, disentangle to a certain extent, and when no further change in their arrangement is possible, their apparent viscosity becomes constant, giving rise to the second Newtonian region.[8,9]

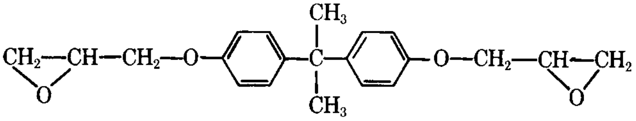
Above the second Newtonian region, an additional non-Newtonian behavior was observed by Ostwald but this is already the region of turbulent flow in which the formation of Taylor vortices takes place.[10]

In our work on some medium and high molecular weight polar fluids that are able to form strong intermolecular bonds and on their solutions in nonpolar solvents, three of the above mentioned phenomena appeared: pseudoplasticity, thixotropy, and rheopexy.

Experimental

Materials used in this work were: PI, a saturated polyester prepared from propylene glycol, phthalic anhydride, and succinic acid in molar ratios 2:1:1 respectively, with an acid number of 39.1; PII, an aliphatic saturated polyester, Dalterol PRI, made by Imperial Chemical Industries; PIII, an unsaturated polyester of the maleic type, mixed with about $^1/_3$ (by weight) of styrene, designated by its manufacturer, American Cyanamid Company, as Laminac 4134. All three polyesters had approximately the same molecular weight of about 2000, determined by cryoscopic measurements.

Also used was the epoxy, Epon 826 (manufactured by Shell Chemical Company), whose structure can be represented by the relatively simple formula:



as the amount of other diepoxides in the resin is very small.[11]

Solvents were toluene, ethylbenzene, dioctyl phthalate, dibutyl phthalate, and butyl acetate, all of them C.P. grade.

The viscometer used, Rotovisco (Haake Co.), was of the rotating type, with cone-and-plate arrangements and equipped with thermostatic and recording facilities.

Results

Most of the experimental work was done on the model polyester PI; the results are shown in Table I. The experiments were carried out in order to find the correlations between the shearing stress and the rate of shear, shearing time, temperature, nature of solvent, and solvent concentration.

As it can be expected, the "goodness" of the solvent is a very important factor in the general behavior of the solutions sheared at a constant rate.

In the case of a good solvent like dibutyl phthalate or dioctyl phthalate, after the initial decrease there is no change of the shear stress during the time of shear, the apparent viscosity η_a is a constant, and the behavior of the fluid is slightly pseudoplastic (Fig. 1).

In solution in a poor solvent like butyl acetate, the polymer precipitates, and the fluid becomes thixotropic. A weak structure builds up on rest and breaks down under shear, and the apparent viscosity drops quickly to a certain value of η_∞ at a constant rate of shear and temperature.

Most interesting results were obtained with "medium" solvents, toluene or ethylbenzene (styrene in Laminac 4134 can be regarded as a medium solvent for the polyester), and in these fluids the rate of shear had a very pronounced influence on the shear stress at constant temperatures. Some flow curves of PI and solutions of PI in toluene are shown in Figure 2. Below a certain limiting rate of shear, after the initial decrease, the shear stress remained constant for a given rate of shear; after interruption of the experiment and its renewal (with the same rate of shear), no time effects

TABLE I
Shearing Stress–Shearing Time–Concentration Relationship at Various Temperatures and Various Constant Rates of Shear for Polyester PI

Temp., °C.	D, sec.$^{-1}$	PI/tol (wt.)	Shearing stress at various shear times, dyne/cm.^{2} $\times 10^{-3}$									τ_{eq}, dyne/cm.^{2} $\times 10^{-3}$ [a]
			0	10 min.	20 min.	40 min.	60 min.	80 min.	100 min.	150 min.	200 min.	
60	2755	80/20	48.40	37.30	50.80	67.80	104.10	140.40	159.80	210.60	232.40	232.40
		60/40	24.20	14.50	21.80	38.70	58.10	92.00	101.60	159.70	193.60	222.70
		40/60	24.20	16.90	21.70	41.20	60.50	70.10	75.00	116.20	157.30	212.00
		20/80	36.30	26.60	49.60	128.30	174.30	210.60	232.40	237.20	—	237.20
60	4133	80/20	19.40	31.00	43.70	60.50	119.80	167.00	196.10	241.90	251.70	251.70
		60/40	24.20	46.00	67.80	113.30	152.50	188.80	210.60	242.00	—	242.00
		40/60	26.60	31.40	55.70	135.30	217.80	246.90	—	—	—	246.90
		20/80	14.50	59.30	90.70	141.60	164.60	184.00	213.00	—	—	213.00
60	8267	80/20	21.80	26.60	48.40	99.20	147.65	198.50	251.70	455.00	479.30	484.10
		60/40	14.50	63.40	91.60	225.10	319.40	387.30	411.30	416.30	—	416.30
		40/60	14.50	150.60	232.40	406.60	426.00	440.50	—	—	—	440.50
		20/80	19.40	348.00	445.40	469.60	—	—	—	—	—	469.60
70	2755	80/20	36.30	30.20	29.00	32.70	48.40	55.70	67.80	80.00	88.30	88.30
		60/40	24.20	26.60	35.10	55.70	75.00	89.50	102.80	115.20	—	115.20
		40/60	24.20	23.00	31.40	65.40	89.50	101.70	107.70	116.20	—	116.20
		20/80	13.10	22.70	56.90	89.50	98.00	101.60	107.70	—	—	107.70
70	4133	80/20	20.60	25.40	33.90	53.30	73.80	86.40	102.90	122.20	124.60	124.60
		60/40	24.20	45.00	70.20	104.10	121.00	130.00	133.10	—	—	133.10
		40/60	14.50	20.50	38.70	77.30	111.30	125.50	128.30	—	—	128.30
		20/80	19.40	106.50	127.10	134.30	135.50	—	—	—	—	135.50

70	8267	80/20	24.20	77.30	159.70	242.00	256.60	—	—	—	—	256.60
		60/40	24.20	89.50	193.60	242.00	—	—	—	—	—	242.00
		40/60	14.50	41.00	89.50	215.40	246.90	—	—	—	—	246.90
		20/80	24.20	128.30	208.60	228.00	—	—	—	—	—	228.00
80	2755	80/20	18.20	21.80	27.80	35.10	42.40	44.70	—	—	—	44.70
		60/40	15.70	21.80	32.70	38.60	43.50	44.70	—	—	—	44.70
		40/60	18.20	21.80	35.10	43.50	—	—	—	—	—	43.50
		20/80	18.10	27.80	41.20	48.10	—	—	—	—	—	48.10
80	4133	80/20	19.40	24.20	38.70	55.70	62.90	—	—	—	—	62.90
		60/40	16.90	26.60	41.20	59.30	65.30	69.00	—	—	—	69.00
		40/60	29.80	29.00	37.50	56.90	64.10	67.80	—	—	—	67.80
		20/80	19.40	67.90	—	—	—	—	—	—	—	67.80
80	8267	80/20	24.20	33.90	50.80	90.70	109.00	117.40	125.80	129.40	—	129.40
		60/40	16.90	55.70	80.40	121.00	125.80	—	—	—	—	125.80
		40/60	16.90	48.40	71.30	114.00	122.20	—	—	—	—	122.20
		20/80	12.10	125.90	134.00	—	—	—	—	—	—	134.00
90	2755	80/20	46.00	62.90	77.50	81.10	84.90	86.10	86.10	—	—	86.10
		60/40	33.90	38.70	47.20	77.50	92.30	86.10	86.10	—	—	86.10
		40/60	19.40	60.50	72.60	84.90	86.10	—	—	—	—	86.10
		20/80	24.20	48.40	70.20	80.00	81.20	81.20	81.20	—	—	81.20
90	4133	80/20	26.60	30.20	36.30	43.50	46.00	46.00	46.00	—	—	46.00
		60/40	16.90	23.00	36.30	43.50	43.50	49.60	49.60	—	—	49.60
		40/60	29.00	33.90	41.20	50.80	50.80	50.80	—	—	—	50.80
		20/80	24.20	21.80	53.90	49.60	49.60	—	49.60	—	—	49.60
90	8267	80/20	24.20	30.20	31.50	33.90	41.20	42.40	35.10	38.70	—	38.70
		60/40	21.80	30.50	26.60	37.50	37.50	37.50	—	—	—	37.50
		40/60	36.30	21.80	26.60	35.10	37.50	37.50	—	—	—	37.50
		20/80	24.20	31.40	32.60	37.50	—	—	—	—	—	37.50

---

[a] Persisting for at least 30 min.

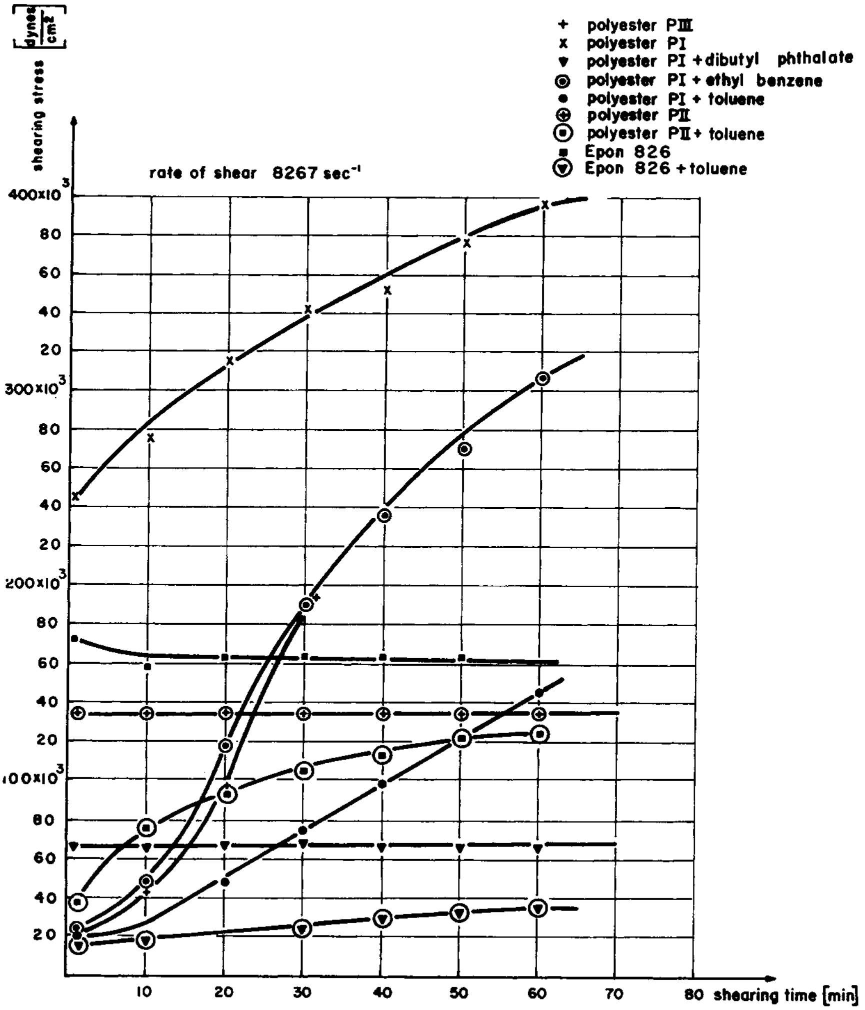


Fig. 1. Shearing stress–shearing time relation for all investigated fluids, rate of shear 8267 sec.$^{-1}$, temperature 60°C.

were observed (Fig. 3); the fluid showed a pseudoplastic behavior. With the increase of the rate of shear, a certain critical rate, characteristic for the fluid, was reached. When the fluid was sheared with higher rates than the critical one, its behavior changed. The shear stress increased with time at any constant rate of shear, and after interruption of the experiment for several minutes and its renewal (with the same rate of shear) no drop of shear stress could be seen; on the contrary, an increase, albeit small, in its value was observed that did not disappear immediately after restoration of the shear. The fluid was clearly rheopectic in its behavior (Fig. 3). On continued shear with the same rate (higher than critical), the stress reached, after a certain time, a pseudoequilibrium value persisting for at least 30 min. (Figs. 3 and 4). After an interruption of the experiment at this stage for a short period (several minutes) and renewal of the shear with the same rate, an increase in the stress was observed which soon dropped under continuous shear to the value observed before the interruption. It seems that during the short time of rest a weak thixotropic structure built up on top of the existing rheopectic one, and the former broke down under the renewed shear. When the shear was interrupted for a long time (24 hr. or more) and then renewed, a strong drop in shear stress was noticed, caused probably by disintegration of the rheopectic structure, proving the process to be at least partially reversible. In experiments with the commercial polyester PIII, the breakdown of the rheopectic structure, followed by a marked drop in the shear stress, was observed after about 32 min. of continuous shearing at the same constant rate (Fig. 1).

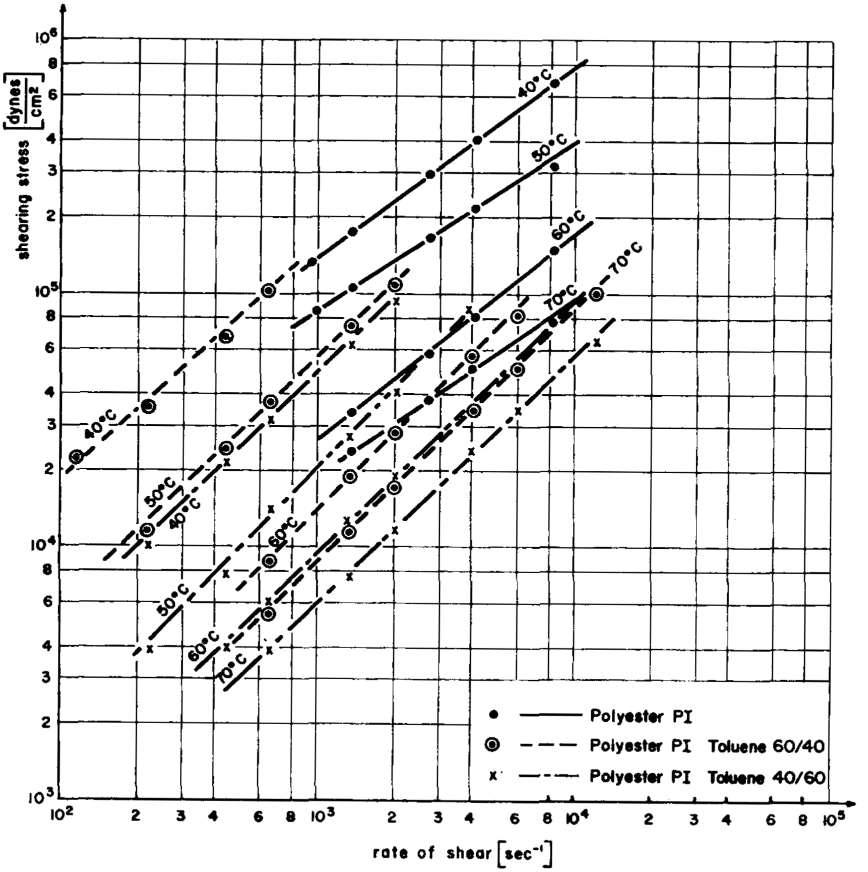


Fig. 2. Flow curves for polyester PI and PI/toluene solutions, temperatures 40, 50, 60, 70°C.

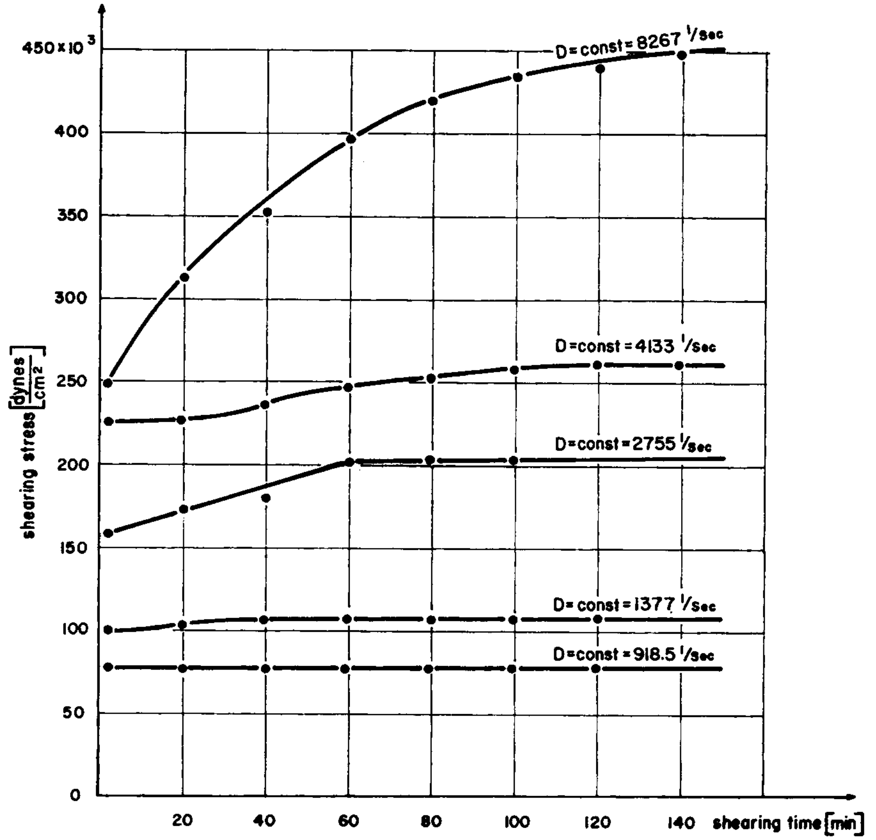


Fig. 3. Shearing stress–shearing time relation for polyester PI at different rates of shear, temperature 60°C.

An increase in the temperature of the experiments carried out at a constant rate of shear above the critical shearing rate had, as it can be expected, a twofold effect on the fluid: the pseudoequilibrium was reached faster, and the apparent viscosity of the fluid at the pseudoequilibrium η_{eq} was lower. The experiments were carried out in two ways: (*a*) series of measurements were made at different temperatures; (*b*) in the same experiment, after reaching the pseudoequilibrium, the temperature was quickly changed (under continuous shear) and kept constant again; in both cases, for the same temperatures the same numerical values for η_{eq} were obtained. The relation between η_{eq} and temperature can be expressed by the simple equation, $\eta_{eq} = A \exp \left\{-Bt\right\}$, where A and B are constants and t is temperature.

At constant temperatures and rates of shear (above the critical rates), the value of the shear stress at pseudoequilibrium τ_{eg} was almost not affected by the amount of the solvent in the investigated fluids (compositions with 0–80% of solvent); it was reached by the different solutions after

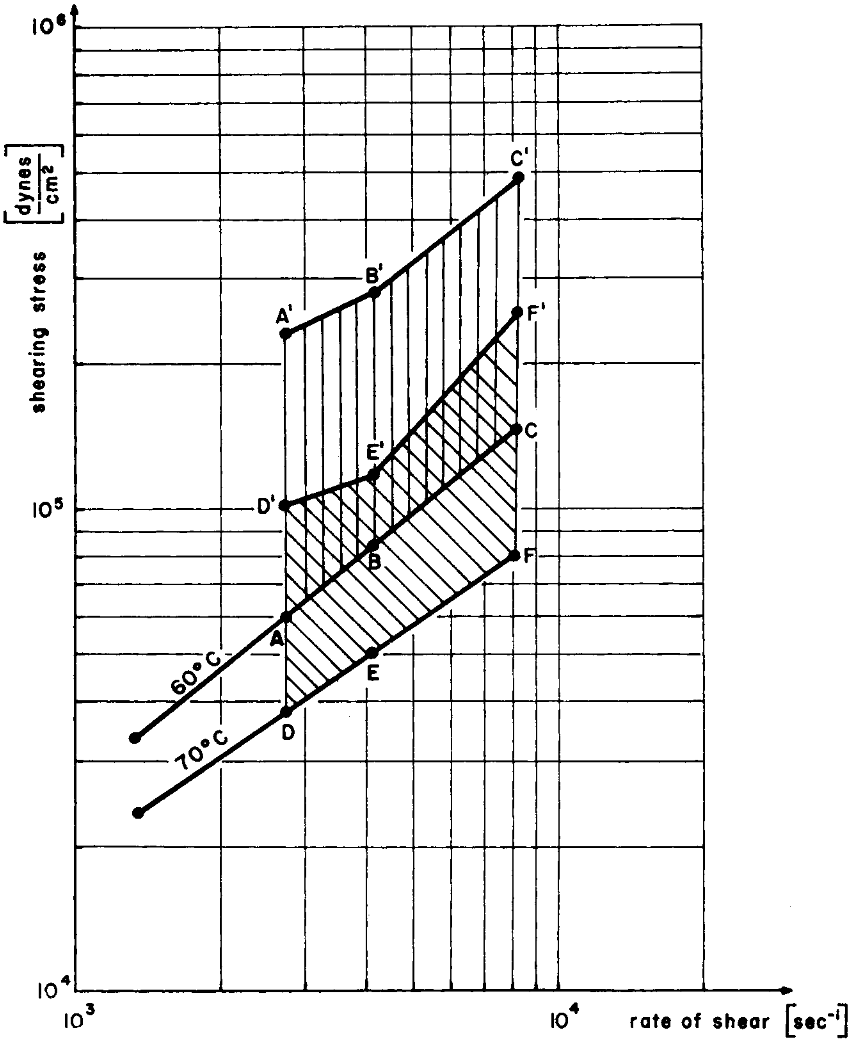


Fig. 4. Flow behavior of polyester PI at 60 and 70°C., rates of shear 2755, 4133, 8267 sec.$^{-1}$: (*A*, *B*, *C*; *D*, *E*, *F*) initial stage. (*A'*, *B'*, *C'*; *D'*, *E'*, *F'*) after the equilibrium was reached.

different times of shearing (Figs. 5–7). The rate of approach to the limiting value of the shearing stress was the fastest for the fluid with the highest solvent content.

All the other products studied showed the behavior described previously in the case of the polyester PI in toluene. The rheopectic structure that built up at the same rate of shear (D = 8267 sec.$^{-1}$) at 60°C., decreased in the following order: PI/ethylbenzene, Laminac 4134, Dalterol/toluene, Epon 826/toluene. In the case of the solventless high molecular weight fluids in the same shearing conditions (D = 8267 sec.$^{-1}$, 60°C.) rheopexy

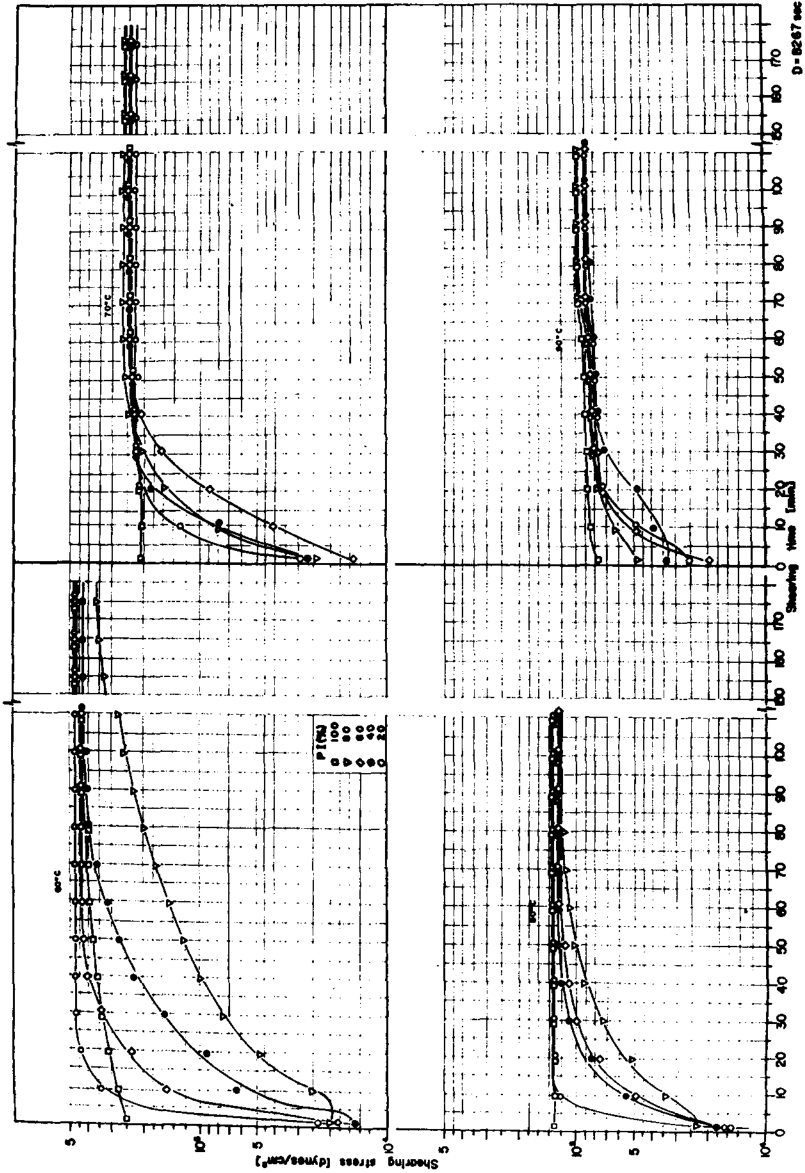


Fig. 5. Shearing stress–shearing time relation for polyester PI/toluene solutions, rate of shear 2755 sec.$^{-1}$, temperatures: 40, 50, 60, 70°C.

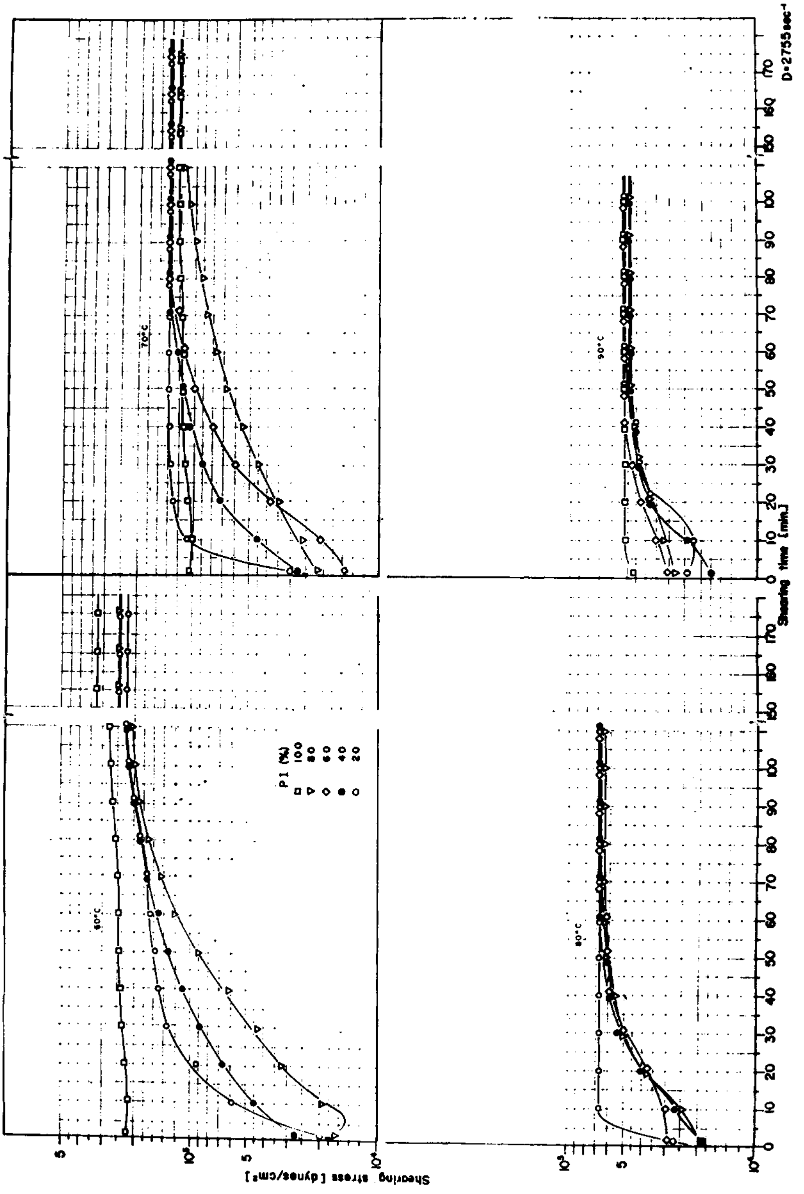


Fig. 6. Shearing stress–shearing time relation for polyester PI/toluene solution, rate of shear 4133 sec.⁻¹, temperatures 40, 50, 60 70°C.

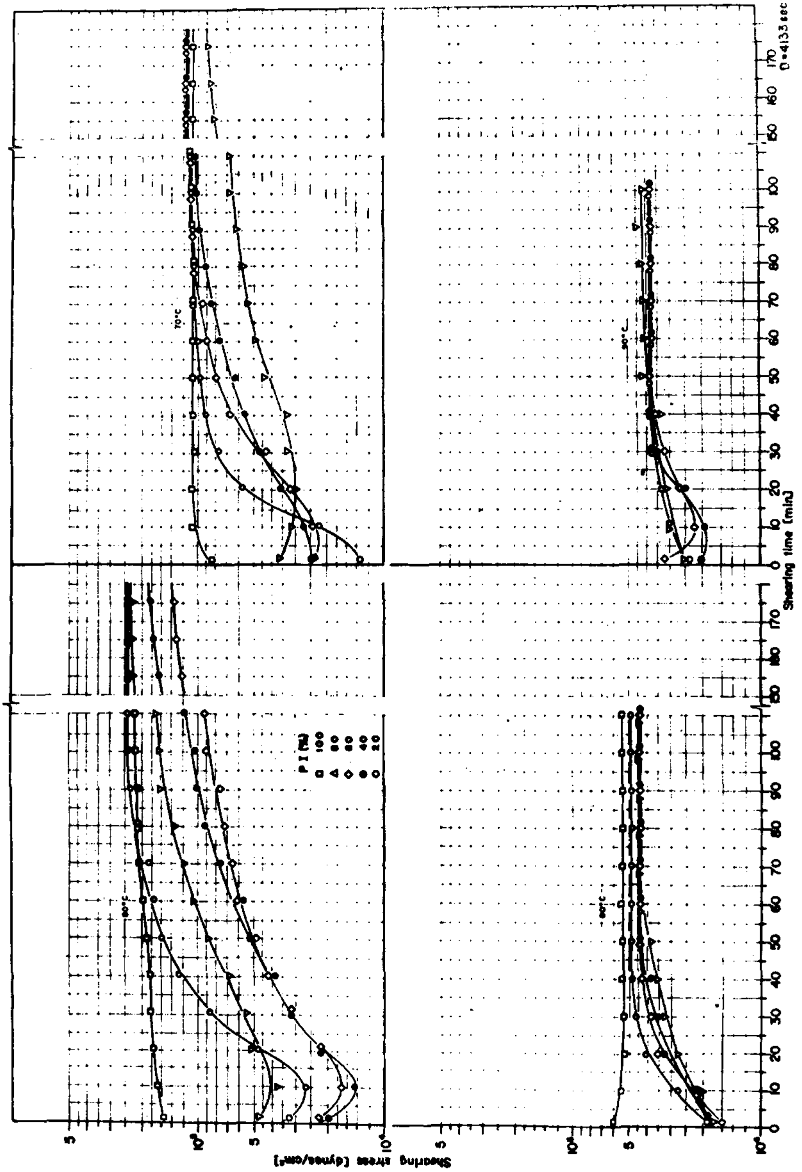


Fig. 7. Shearing stress-shearing time relation for polyester PI/toluene solutions, rate of shear 8267 sec.$^{-1}$, temperatures 40, 50, 60, 70°C.

was observed only in PI; Dalterol and Epon 826 showed no time-dependent behavior (Fig. 1).

Discussion

According to Born and Green,[12] the viscosity of a fluid is determined by contributions from two basic mechanisms: from the "kinetic" contribution produced by thermal motion of liquid particles resulting in transfer of momentum from the faster-moving layers to the adjacent slower-moving ones and from the action of the intermolecular forces between the liquid particles.

The general problem of solvent–polymer interaction was treated earlier by different investigators,[13] but mostly in cases of relatively low polymer concentrations of nonpolar polymers with much higher molecular weights than the fluids used in this study.

The rheological behavior of concentrated solutions and suspensions of the polymers investigated in this work depends very strongly on the nature of the solvent. Several models will now be discussed in order to explain this behavior.

In the case of a polyester dissolved in a good solvent, the fluid showed in all our experiments a pseudoplastic behavior with very short first Newtonian and first non-Newtonian regions. This could be explained by assuming that the shielded polar groups of the solvated polyester molecules were not able to interact with each other, and therefore no intermolecular rheological structure could be build up, neither in the field of shear nor at rest after the shear was interrupted; the interaction between the molecules was purely hydrodynamic.

In the second case, a polyester in a poor solvent, the behavior of the fluid was thixotropic; the rheological structure that built up at rest was destroyed by shear, and the time effect was clear. This phenomenon can be explained easily in the following way. As the shielding of the polar groups of the polyester by the poor solvent molecules is very inefficient, the forces of attraction between the particles are exceeding the dispersion forces between them which are due to Brownian motion. The particles are approaching each other by overcoming the energy barrier created by the Brownian motion, and weak secondary links are formed between them, giving a coagulation structure; the mechanism of the process was described and explained by Derjaguin[14] and Rehbinder.[15,16] As the links are localized only at a very few points of the relatively long rod-shaped molecules of the polyester, a weak network structure is formed, defined by Rehbinder as a reversible thixotropic coagulation framework.[16] The most complicated behavior was shown by the bulk polyester and its solutions in a medium solvent like toluene, ethylbenzene, or styrene (in the commercial Laminac 4134). As mentioned already in the experimental part, below a certain critical rate of shear, the investigated low polymers and their solutions were pseudoplastic. With the increase of the rate of shear above the critical value, the behavior of the fluids changed, and time effects connected with the formation of rheological structures were noticed.

At the early stages of the experiment, carried out with a shear rate higher than the critical one, a rheopectic, or negative thixotropic, structure built up quickly; the rate of growth of the structure decreased with time until a pseudoequilibrium in the relation between the shear stress and time was reached. If the shear was interrupted for a few minutes before the pseudoequilibrium was reached and then renewed at the same rate, it could be observed that during the rest period the structure strengthened and the shear stress increased and continued to increase on further shear. Interruption of the shear for several minutes after the pseudoequilibrium was reached caused again a strengthening of the structure during the rest period, but on further shearing with the same rate, the shear stress soon fell to the pseudoequilibrium value, indicating this time a breakdown of the struture formed during the rest period. Based on these observations, the following explanation is suggested for the changes occuring in the fluids investigated, when subjected to shear under isothermal conditions.

At relatively low shear rates the systems disperse the shearing forces without undergoing any changes, and no time effects are observed. With the increase of the rate of shear above a certain critical value, the energy introduced into the system is not just dispersed in the form of heat but also effects the equilibrium in intermolecular or perhaps also intramolecular bonding between the molecules. The distances between some of the polyester molecules aligned in the field of shear decrease, and the linear molecules build anisodiametric agglomerates, mostly due to the formation of strong polar and hydrogen bonds between them. These agglomerates can be seen as quasicrystallites in solution.[17] As the shielding of the polar polyester groups by the mediocre solvent is only slight, due to weak interaction, solvent molecules are probably "squeezed out" in the field of shear from the space between the approaching and interacting polyester molecules. A certain amount of energy is introduced by shear so as to affect the thermodynamic equilibrium in the fluid and to build the new structures with a higher free energy content. The quasicrystallites, oriented in the field of shear, can be held together by more intermolecular forces, probably of weaker nature than the ones building the quasicrystallites, thus forming a larger network structure. A somewhat similar explanation for negative thixotropy in a different system was offered by Eliassaf, Silberberg, and Katchalsky,[5] and the model corresponds to the general definition given by Weltmann[16] that in rheopectic materials an almost perfect orientation of anisodiametric particles in the field of shear is necessary. The relative ease of straightening of the macromolecules in the field of shear can be attributed to their limited length and to the internal stiffness of the polyester chains.

As the shearing forces are acting also in the opposite direction, by breaking intermolecular bonds, a dynamic pseudoequilibrium is established and persists under unchanging conditions (rate of shear, temperature, etc.)

in the system under shear for a long time. The assumption of such a model seems to be supported by a further observation made when the experiment was interrupted for short periods (of several minutes) after the shear stress plateau was reached. Immediately after the renewal of the shear with the same rate, a slight increase in the shear stress was noticed, and after a short time of shear the stress dropped again to the pseudoequilibrium value. During the period of rest, a weak thixotropic structure of reversible coagulation character built up in the fluid, due to formation of some additional weak intermolecular bonds, and this structure was destroyed after the restoration of shear.

In case the experiments were interrupted for a short period (several minutes) before the pseudoequilibrium was reached, a slight increase in shearing stress was also observed immediately after the renewal of the shear with the same rate, but the shear stress continued to grow without drop until the pseudoequilibrium value was reached. This can be due to such a fast rheopectic build-up with the renewal of shear that the destruction of the weak thixotropic structure could not be observed.

The appearance of the thixotropic structure in addition to the rheopectic (or antithixotropic) one can be explained in the following way. With the formation of quasicrystallites, the size and the shape of the fluid particles is different than before, thus changing the balance between the dispersion and attraction forces responsible for coagulation[14–16] and giving reversible thixotropic coagulation structures.[16] The same conclusions can be reached by considering also the change in the "goodness" of the solvent with relation to the solute when the quasicrystallites start to build up.

Likewise, in the case of the bulk polyester, an amount of energy has to be supplied in order to change the existing equilibrium, to orient the molecules, and to build the polymer quasicrystallites with a higher free energy content. Until this amount of energy is supplied, the polyester behaves as a weakly pseudoplastic fluid. Once the critical rate of shear is exceeded and the shear continues, all the phenomena described earlier, rheopexy, pseudoequilibrium stress at a constant rate of shear, and thixotropy, can be observed in the system.

The experiments show that at constant temperatures and rates of shear above the critical rate, the shear stress at equilibrium was almost the same for different compositions of the polyester PI and solvent (amounts of solvent from 0 to 80%). This behavior indicates that the internal stiffness and resistance to shear of the concentrated solutions of the polymer during the experiment as well as the pseudoequilibrium between the building up and breaking up of the structure due to shear in all cases reaches values that are not very different. This phenomenon is not clear, but it can perhaps be explained by assuming that up to the stage investigated in our work only a small part of the polymer molecules participates in the process of building the rheopectic network structure. All the other polyester particles, together with the solvent molecules, do not contribute to the increase of the resistance of the system to shear.

One more point has to be mentioned in this discussion, viz., the remarkable strength of some of the investigated rheopectic structures. The phenomenon of rheopexy described here seems to be strictly connected with the length, bulkiness, and stiffness of the molecule. By limiting the number of possible chain conformations through introduction of stiff zones into the narrow linear molecules, the lifetime of the quasicrystallites is extended, and the rheopectic structures are becoming stronger. These assumptions are supported by the experimental results obtained with the solventless aliphatic saturated polyester, that showed at all rates of shear tested only a slightly pseudoplastic behavior. On the other hand, the two remaining polyesters with approximately the same average molecular weights, one with maleic, the other with phthalic acid groups in the chain, showed above critical rates of shear all the phenomena described earlier, and their rheopectic structures persisted for long times after interruption of the shear.

A solution of the aliphatic saturated polyester in toluene showed rheopectic behavior when sheared at a high rate, but the structure was weaker than the structures of corresponding solutions of the two other polyesters, although the same conditions were applied. A similar behavior was shown also by Epon 826 with a much lower molecular weight than the polyesters. The epoxy compound (solventless) was slightly pseudoplastic at all investigated rates of shear. The concentrated toluene solution of Epon 826 showed rheopectic behavior at a rate of shear of 8267 sec.$^{-1}$, but the rate of the build-up and the strength of the structure were very low. The whole problem of the strength of the rheopectic structure is under further investigation.

References

1. Weltmann, R. N., in *Rheology*, Vol. III, F. R. Eirich, Ed., Academic Press, New York, 1956, (a) p. 189; (b) p. 216.
2. Wilkinson, W. L., *Non-Newtonian Fluids*, Pergamon Press, London, 1960.
3. Ostwald, W., *Kolloid-Z.*, **38,** 261 (1926).
4. Reiner, M., *Deformation Strain and Flow*, Lewis, London, 1960, p. 243.
5. Eliasaff, J., A. Silberberg, and A. Katchalsky, *Nature*, **176,** 1119 (1955).
6. Crane, J., and D. Schiffer, *J. Polymer Sci.*, **23,** 93 (1957).
7. Merrill, E., *Modern Chemical Engineering*, Vol. I, A. Acrivos, Ed., Reinhold, New York, 1963, p. 141.
8. Ostwald, W., *Z. Physik. Chem.*, **A111,** 62 (1924).
9. Philippoff, W., *Viscositat der Kolloide*, Steinkopf, Dresden, 1942, p. 113.
10. Taylor, G. J., *Phil. Trans.*, **A233,** 289 (1923).
11. Shell Chemical Co., *Epon Resins For Structural Uses, Shell Tech. Bull.*, Sc-60-39 Rev.
12. Born, M., and H. S. Green, *Proc. Roy. Soc.* (*London*), **A188,** 10 (1946).
13. Frish, H. L., and R. Simha, in *Rheology*, Vol. I, F. R. Eirich, Ed., Academic Press, New York, 1956, p. 564.
14. Derjaguin, B. V., *Trans. Faraday Soc.*, **36,** 203, 730 (1940).
15. Rehbinder, P. A., and Mikhailov, N. W., *Rheologica Acta*, **1,** 1361 (1961).
16. Rehbinder, P. A., *Discussions Faraday Soc.*, **No. 18,** 157 (1954).
17. Edsall, J. T., *Advances in Colloid Science*, Vol. I, E. O. Kraemer, Ed., Interscience, New York, 1942, p. 313.

Résumé

De nombreux milieux de même que les fluides polaires de hauts poids moléculaire montrent un comportement rhéopectique lorsque la vitesse de cisaillement à laquelle ils sont soumis dépasse un certain niveau. Ceci s'observe pour certains polyesters et certaines résines époxydées de même que pour leurs solutions dans des solvants-non-polaires. Les expériences ont été effectuées dans un viscosimètre rotatif à cône et à plateau. On propose l'explication suivante pour le comportement rhéopectique: lorsqu' on dépasse une certaine vitesse de cisaillement les macromolécules polaires s'alignent suivant le champ des forces de cisaillement et forment des paracristaux et une structure rhéologique réticulée par suite de forces intermoléculaires. Comme il y a simultanément formation et rupture de ces structures dans le champ de cisaillement, on atteint un état de pseudo-équilibre. On a trouvé qu'un renforcement thixotropique des structures existantes se produisait lorsqu'on interrompait l'expérience au stade du pseudoéquilibre pendant un instant très court. Lorsqu'on reprend l'expérience, la tension décroît et reprend sa valeur d'équilibre primitive. Lorsqu'on interrompt le cisaillement pendant des périodes relativement longues (heures, jours), on observe la disparition des structures rhéopectiques.

Zusammenfassung

Einige polare Flüssigkeiten mit mittlerem und hohem Molekulargewicht zeigten bei Einwirkung von Scherkräften oberhalb einer bestimmten Schubgeschwindigkeit ein rheopektisches Verhalten. Diese Beobachtung wurde an einigen Polyestern, einer Epoxyverbindung und an konzentrierten Lösungen dieser Stoffe in unpolaren Lösungsmitteln gemacht. Die Versuche wurden in einem Rotationsvikosimeter mit Kegelplatteneinrichtung gemacht. Folgende Erklärung wird für die beobachtete Rheopexie gegeben: Oberhalb einer kritischen Schubgeschwindigkeit bilden die polaren Markromoleküle nach Ausrichtung im Scherfeld auf Grund der intermolekularen Kräfte Quasikristallite und eine rheologische Netzwerkstruktur. Durch das gleichzeitige Auftreten eines Strukturzerstörungsprozesses im Scherfeld wird ein Pseudogleichgewichtszustand erreicht. Bei Unterbrechung der Versuche in einem solchen Pseudogleichgewichtszustand für kurze Zeit trat eine thixotrope Verfestigung der bestehenden Struktur auf; bei neuerlicher Einwirkung der Scherung sank die Spannung auf ihren Wert vor der Unterbrechung ab. Bei Unterbrechung der Scherung für längere Zeit (Stunden, Tage) wurde ein Zusammenbruch der rheopektischen Struktur beobachtet.

Received April 28, 1965