

The Development of Molecular Orientation during Formation of Cellulose Film from Viscose*

V. C. HASKELL and D. K. OWENS

*Cellophane Research and Development Laboratory, E. I. du Pont de Nemours & Company, Inc.,
Richmond, Virginia*

I. INTRODUCTION

Molecular orientation is known to have a profound effect on the mechanical properties of high polymer systems generally and of regenerated cellulose specifically. In rayon, maximum tensile strength is achieved only by stretching the fibers to get a high degree of alignment of the cellulose chains along the fiber axis. The mechanism by which orientation is developed in cellulose has been studied by Kratky,¹ P. H. Hermans,² and J. J. Hermans.³ In their work, calculations were made of the effect of the amount of stretching on orientation, first with a model of rigid rods suspended in a fluid matrix and then with various types of network structure models. To check the theory, an extremely useful technique was developed for preparing model filaments of regenerated cellulose which were isotropic. Stretching experiments on isotropic model filaments showed that the behavior of gel cellulose filaments is closer to that of a network structure than to the fluid matrix model.

In principle, the above results should be applicable to the problem of explaining how molecular orientation develops in a regenerated cellulose film. To elucidate this process-structure relationship, a more complete description of orientation in cellophane was sought with emphasis on point-to-point variations within the sheet. An explanation of the observed structure was then formulated in terms of the mechanism of coagulation and the forces acting on the web during and after coagulation. Optical methods based on birefringence was chosen for this study.

Figure 1 illustrates the technique by which molecular orientation was studied in three dimen-

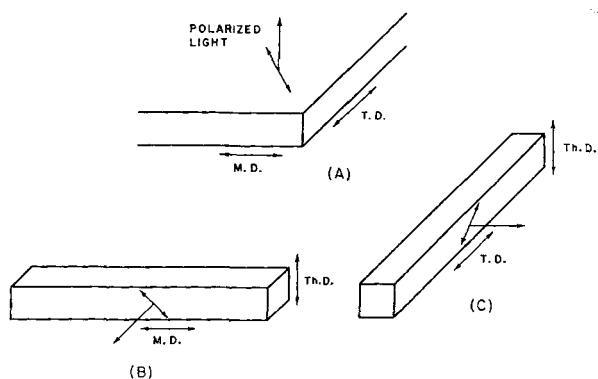


Fig. 1. Diagrammatic representation of cellophane behavior in polarized light.

sions. In Figure 1A, plane-polarized light is shown passing perpendicularly through the sheet. The plane of polarization is inclined 45° to the machine direction, so that components are vibrating in the machine and transverse directions. The optical retardation so measured is related to the difference in the degree of alignment of molecules in the machine and in the transverse directions.

In Figure 1B is illustrated a cross section of film cut in the machine direction. Polarized light passing transversely through the section has components in the thickness and machine directions. Optical retardation in this case is a measure of preferential alignment in the machine direction over the thickness direction. Similarly, in the cross section cut in the transverse direction, as shown in Figure 1C, information is obtained about preferential alignment of molecules in the transverse direction relative to the thickness direction.

II. EXPERIMENTAL

Measurements of optical retardation with light passing through the sheet perpendicularly were straightforward. For measurements in the other

* Paper presented at the 137th National American Chemical Society Meeting, Division of Cellulose Chemistry, Cleveland, Ohio, April 8, 1960.

directions it was necessary to embed strips of cellophane in wax (Fisher Tissuemat; m.p. 60–62°C.), and cut cross sections of accurately known thickness with a microtome, care being taken to minimize distortion during cutting and handling.

The cross sections were flattened and secured to the microscope slide by applying a thin layer of partly cured phenol-formaldehyde resin (Bakelite BRL-1100) from 20% acetone solution to the slide. The sections were transferred to this adhesive layer, rolled flat on a warming table, and then dewaxed in xylene. The sections were then mounted in a synthetic mountant (Harleco synthetic resin) and covered with a #1 cover glass. The mounting medium eliminated surface detail and microtome scratches and permitted clearer pictures to be made of the retardation profile. With a 57 \times , N.A. 0.85 dry objective in the polarizing microscope and a graduated quartz wedge compensator (American Optical Co., Catalog #555) replacing the ocular, the cross section was brought into focus, and the polarizer, specimen, and wedge were oriented for optimum resolution of the zero-order extinction band in the film. Photographs were then made at 350 \times on 2 $\frac{1}{4}$ in. \times 3 $\frac{1}{4}$ in. cut film.

III. RESULTS

A typical curve of optical retardation of dynamically cast film as a function of position across the sheet with light passing perpendicularly through the sheet is shown in Figure 2. It is seen that the

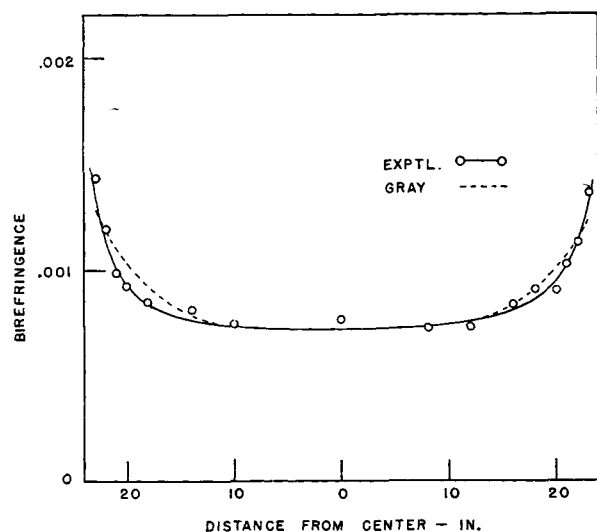


Fig. 2. Birefringence as a function of position across cellophane sheet.

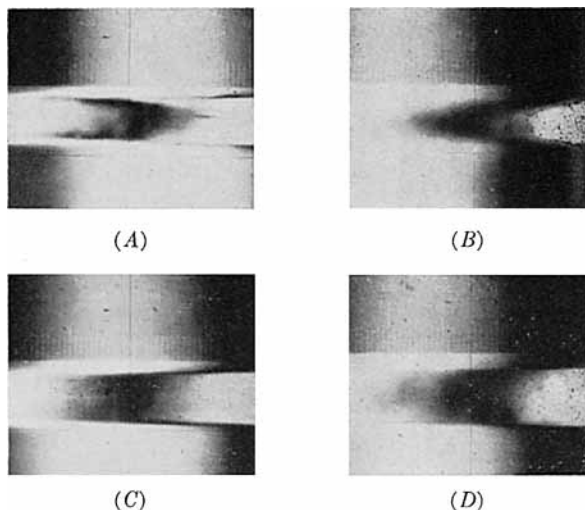


Fig. 3. Microscopic appearance of cross-sections of (top) dynamically and (bottom) statically cast cellophanes: (A), (C) cut parallel to machine direction, viewed transverse; (B), (D) cut transverse, viewed in machine direction.

minimum value of optical retardation occurs in the middle of the sheet. The retardation increases, at first slowly, then more rapidly as the extreme edge of the sheet is approached. Gray,⁴ reporting similar observations, earlier stated that the increase in birefringence from center to edge is proportional to the fourth power of the distance from the edge, the proportionality constant depending on the forces causing transverse shrinkage during sheet formation and drying. The results obtained in this study do not follow exactly the relationship postulated by Gray but are in reasonable agreement.

It has been found that the optical retardation value as measured depends upon the extent of transverse shrinkage which has occurred during processing. As a consequence of the extra transverse shrinkage occurring near the edges of the sheet, it is necessary to extrude a web of viscose which is thinner near the edge of the sheet than in the center. The excess shrinkage near the edges can be explained qualitatively by the observation that the film in the center of the sheet is restrained by film on both sides, whereas that near the edge is subjected to forces only on one side.

Figure 3 shows the appearance of cross sections of cellophane prepared and viewed as described above.

Figure 3A is a section cut parallel to the machine direction and viewed with light passing through the section in the transverse direction. This figure shows that the molecular orientation in the machine

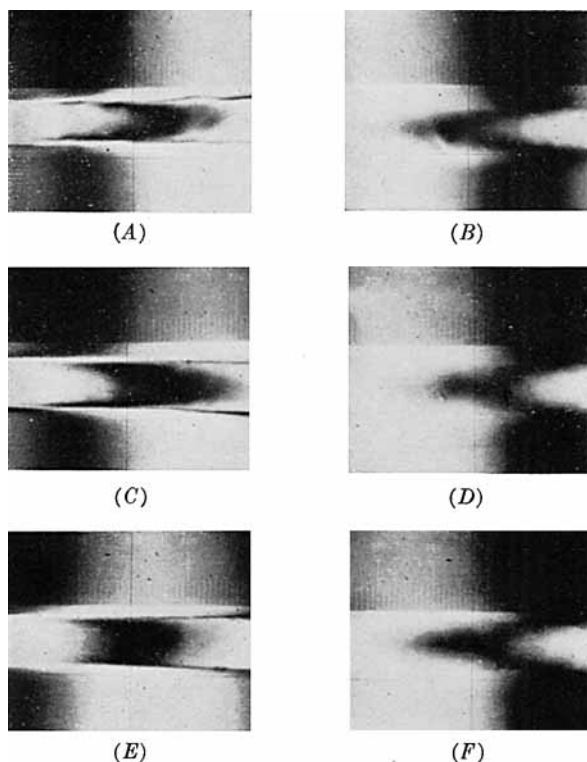


Fig. 4. Microscopic appearance of cellophane cross-sections as a function of casting speed: (A), (B) speed = 2.4; (C), (D) speed = 1.8; (E), (F) speed = 1.0. (A), (C), and (E) are MD sections; (B), (D), and (F) are TD sections.

direction is higher in the surface layers than in the center layers. Figure 3B shows that transverse orientation is lower in the surface than in the center layers. Figures 3C and 3D are similarly cut cross sections from a film cast on a glass plate by essentially the same coagulating bath and viscose

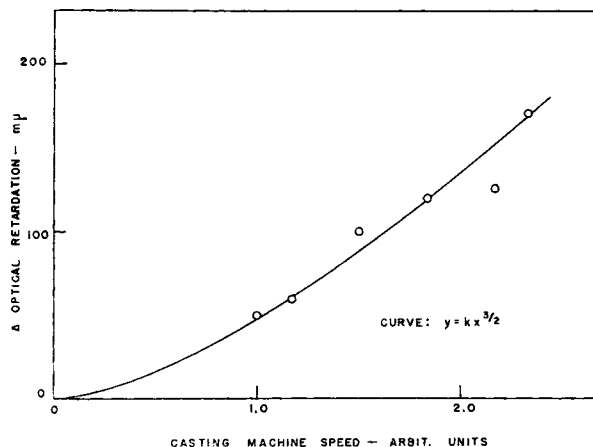


Fig. 5. Cross-section surface-to-center optical retardation difference vs. casting speed.

as with the dynamically cast film and dried with shrinkage of area restrained. In these cross sections there is negligible difference between surface layers and center layers. However, some difference exists between cross sections cut in the two directions of the sheet.

Figure 4 shows a series of cross sections cut from experimental film cast at different speeds on the casting machine. These cross sections were cut from near the center of the dynamically cast sheet. It is apparent that the curvature of the retardation profile in sections cut in the machine direction becomes greater as the casting speed increases. From such pictures as these, measurements of optical retardation in the surface and center layers can be made, and the difference can be correlated with casting speed. Such a correlation is shown graphically in Figure 5. A close fit is obtained with a curve showing dependence on the three-halves power of the casting speed.

Another variable of dynamic casting which might be expected to affect these profiles is the thickness of the slot through which viscose is extruded. Table I shows data from cross sections of film made with slot openings varied over a three-fold range. The small differences in optical retardation realized indicated a rather small effect of this variable under the conditions of the test.

TABLE I
Effect of Hopper Opening on Retardation Profile of Cellophane

| Hopper opening, arbitrary units | Optical retardation, mμ |
|---------------------------------|-------------------------|
| 1 | 100 |
| 2 | 120 |
| 3 | 140 |

IV. FLOW BIREFRINGENCE

Before the development of molecular orientation can be fully explained it is necessary to determine how much shear-induced orientation resulting from flow through the extrusion slot is frozen into the film upon coagulation. An extrusion die was constructed from Lucite (Du Pont's trademark for its acrylic resin) so that shear-induced orientation could be observed and measured in the flow channel. This die is illustrated in Figure 6. Viscose of about 50 poises viscosity was pumped through the die at various pressures. Readings of optical retardation were obtained with light passing perpendicularly through the extrusion channel at

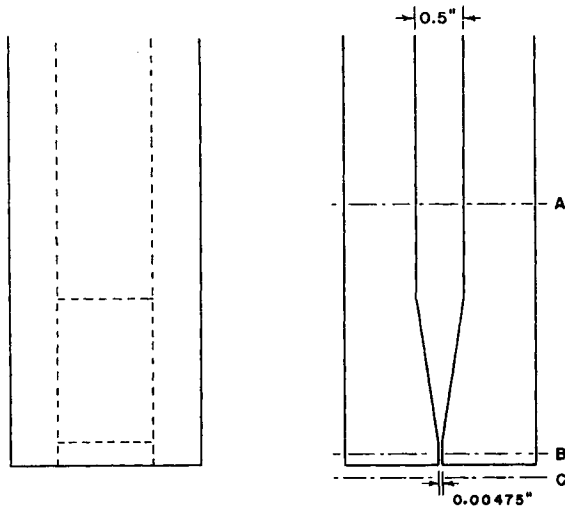


Fig. 6. Viscose extrusion die.

three different points (marked A, B, and C in Fig. 6). Figure 7 shows three curves corresponding to the three positions, in which optical retardation is measured against block pressure in psig. Within the extrusion channel, very little difference was seen in the curves obtained at different widths of channel. It is also apparent that upon leaving the die the flow birefringence disappears very rapidly. At $\frac{1}{8}$ in. from the extrusion orifice the birefringence disappeared completely even at the maximum speed of the experiment (162 m./min.). In other words, it appears that flow birefringence induced by shear in the extrusion die disappears in one-thousandth of a second or less upon extrusion into air. It therefore seems

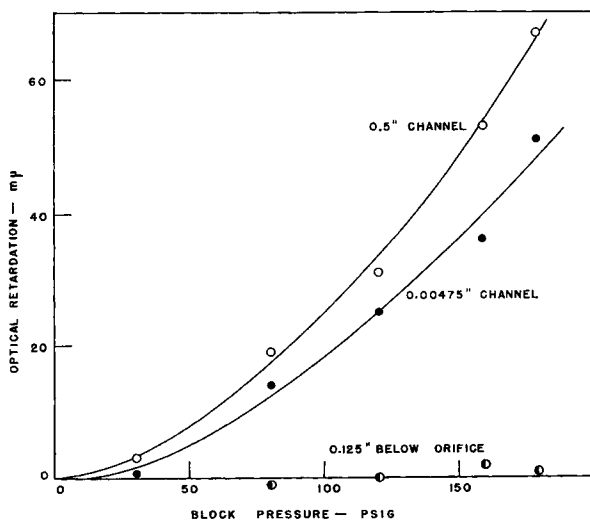


Fig. 7. Flow birefringence as a function of extrusion pressure for different points in extrusion die.

improbable that flow birefringence contributes materially to the orientation induced in the dynamically cast sheet.

V. OPTICAL RETARDATION AND GEL STRETCHING

The network theory of stretching suggests a curve between a straight line and slightly concave upwards describing the relation between optical retardation and the amount of stretching of the film in gel form.⁵ Figure 8 shows the data obtained upon stretched samples of cellophane gel film originally 1 in. wide and 3 in. long and maintained wet throughout the measurements. The approximately linear relation is in accord with the theory and makes possible the calculation of the amount of stretching corresponding to measured amounts of retardation.

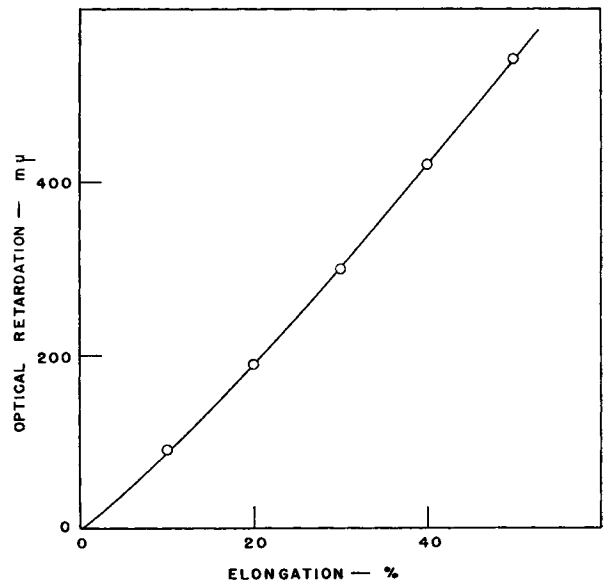


Fig. 8. Optical retardation as a function of elongation for gel cellophane.

VI. RATE OF COAGULATION

In order to reach a plausible explanation for the development of molecular orientation, however, some knowledge about the rate of coagulation and the physical state of the gel at various distances from the extrusion die is necessary. A study of the diffusion rate of acid coagulating bath into viscose was undertaken in the following manner. A wedge-shaped layer of viscose was metered onto a glass plate which had been marked into equally spaced intervals perpendicular to the wedge axis. The plate was partly immersed in coagulating bath

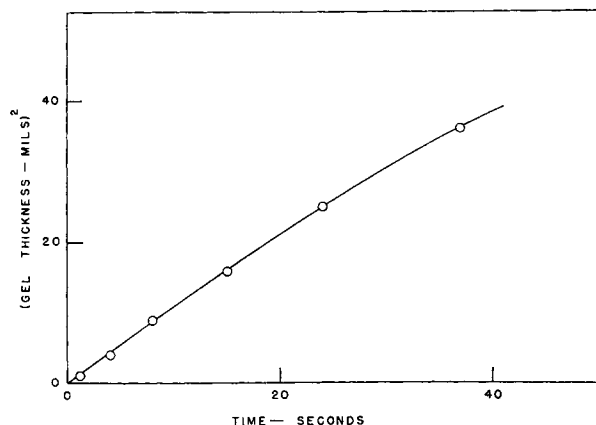


Fig. 9. Coagulation rate of viscose as a function of thickness.

at room temperature with the viscose side down. The viscose had been previously colored with 0.3% Bromcresol Purple. By means of this indicator, it was possible to follow the movement of the color boundary from the thin edge of the viscose layer to the thick edge as the acid penetrated it and to record the times required for equal distance intervals. Measurements of gel film thickness versus distance from the edge showed that the film had a uniform taper. A plot could then be made of acid penetration versus time. This plot is shown in Figure 9. It was found that an approximately linear correlation was obtained by plotting distance squared versus time. This is not an abnormal result for a diffusional process. Its significance is that the coagulation rate is initially rapid but slows down with time. Therefore, the forces acting upon the cellulose gel in the early stages of coagulation are important in determining the shape of the orientation profile.

VII. SUMMARY AND CONCLUSIONS

These observations suggest the following mechanism for the development of molecular orientation in dynamically cast cellophane. Figure 10 is a diagrammatic representation of viscose undergoing extrusion and coagulation. As the viscose is forced through the extrusion orifice, orientation of the molecules in the direction of shear is induced, but this dies out so rapidly that its effect on film orientation can be neglected. As acid penetrates the viscose, a sharp pH front is postulated. Although it is possible that there may be a zone where coagulation has taken place but regeneration is incomplete, it is assumed in this case that this zone is very narrow, so that the partly coagulated sheet

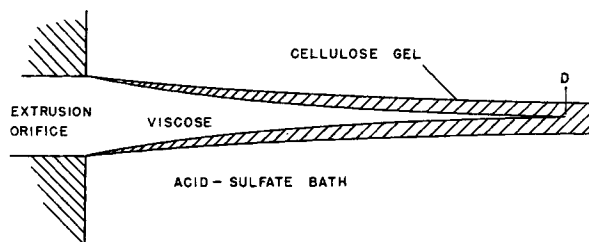


Fig. 10. Diagram of the extrusion and coagulation of viscose.

consists essentially of only two phases, viscose in the interior enclosed by a sheath of regenerated cellulose gel. From the instant the gel is formed, it is subjected to forces which are tending to distort it. The structure would shrink isotropically, but is prevented from doing so by the restraining action of the rolls supporting the film and by the forces of tension required to overcome the drag of the treatment baths and to draw the film down to the proper thickness.

As a consequence of these unbalanced forces, the film necks down in width. The greatest portion of the neck-down occurs during coagulation and regeneration. The structure of the film is altered in two ways by the neck-down. Transverse shrinkage during coagulation reduces the transverse orientation of molecules in surface layers compared with interior layers, producing a curved orientation profile of the type observed in transverse cross sections of cellophane. Also, the processing of film over rolls driven at essentially constant speed minimizes shrinkage in the machine direction, so that molecules tend to be aligned in this direction. The transverse shrinkage is resisted by the restraining action of the rolls of the machine during wet treatment and drying. This restraining action is more effective in the center of the sheet than near the edges, so that the machine orientation tends to be higher near the edges. The curved orientation profile observed in the machine direction cross sections appear to result from the application of machine direction tension to the partly coagulated film. Since coagulation proceeds from the surface inward, the surface layers are exposed to the viscous friction of the coagulating bath for a longer time and with greater intensity. Statically cast cellophane film made on glass plates showed only uniplanar orientation and no significant difference between surface and center layers as expected.

Molecular orientation in cellophane can then be described as uniplanar, combined with a degree of uniaxial orientation in the machine direction.

Variations in the degree of uniaxial orientation are seen across the sheet and also through the sheet as shown by cross sections.

References

1. Kratky, O., *Kolloid Z.*, **64**, 213 (1933); *ibid.*, **84**, 149, 268 (1938).
2. Hermans, P. H., and J. de Booy, *Kolloid Z.*, **88**, 73 (1939).
3. Hermans, J. J., *Flow Properties of Disperse Systems*, Interscience, New York, 1953, p. 108 ff.
4. Gray, R. C., *J. Soc. Chem. Ind. (London)*, **63**, 241 (1944).
5. Hermans, J. J., *op. cit.*, p. 109.

Synopsis

The distribution of molecular orientation in cellophane and its correlation with processing conditions have been studied by means of optical retardation measurements. With thin sections of cellophane cut with a standard microtome edge views were obtained, and it was possible to measure optical retardation profiles of the sections. This yielded information about the variation of molecular orientation in different layers of the film. In lanes near the edge of the machine-cast sheet the machine direction orientation was higher than in center lanes. In layers near the surface, machine direction orientation was higher, and transverse direction orientation was lower than in center layers. Studies of shear induced orientation in viscose indicated that this did not persist long enough to contribute to the structure of cellophane. The distribution of molecular orientation in cellophane was explained in terms of the forces acting on the web during and after coagulation and regeneration. These include the viscous drag of the treatment baths, the internal friction as the viscose is drawn outside the extrusion die, the tendency of the film to shrink during its formation and drying, and the tenting action of machine rolls.

Résumé

On a étudié la distribution de l'orientation moléculaire dans le cellophane et sa corrélation avec les conditions de travail au moyen des mesures de retard optique. Avec des minces coupes de cellophane obtenues au moyen d'un microtome standard, on a obtenu des vues de tranches et il a été possible de mesurer de profil la retard optique dans

les coupes. Ceci a fourni des informations concernant la variation de l'orientation moléculaire dans les différentes couches du film. Dans les régions situées au bord du tranchant de la machine, l'orientation de direction de la machine était plus élevée qu'au centre. Dans les couches près de la surface, l'orientation, de la direction par la machine était plus grande et l'orientation de la direction transverse était plus faible que dans les couches centrales. Des études de l'orientation induite par pression dans le viscose indiquaient que celle-ci ne persistait pas assez longtemps que pour intervenir dans la structure de la cellophane. La distribution de l'orientation moléculaire dans la cellophane s'explique en termes de forces agissant sur le tranchant pendant et après coagulation et régénération. Ceci inclut le frottement visqueux des bains de traitement, les frictions internes lorsque la viscose est poussée au travers des trous d'extrusion, la tendance des films à se rétrécir durant leur formation et leur séchage et l'action d'étendage des rouleaux de la machine.

Zusammenfassung

Die Verteilung der Molekülorientierung in Cellophan und ihre Beziehung zu den Verarbeitungsbedingungen wurde mittels optischer Retardierungsmessungen untersucht. An dünnen Cellophanschnitten, die mit einem Standardmikrotom hergestellt wurden, wurden Kantenansichten erhalten und es war möglich die optischen Retardierungsprofile der Schnitte zu messen. Das lieferte Angaben über die Änderung der Molekülorientierung in verschiedenen Filmschichten. In Bereichen nahe der Kante des maschinen-gegossenen Filmes war die Orientierung nach der Maschinenrichtung höher als in zentralen Bereichen. In Schichten nahe der Oberfläche war die Orientierung in der Maschinenrichtung höher und Orientierung in der Querrichtung niedriger als in zentralen Schichten. Untersuchung der scherungsinduzierten Orientierung bei Viskose zeigte, dass diese nicht lange genug bestehen blieb, um zur Struktur von Cellophan beitragen zu können. Die Verteilung der Molekülorientierung in Cellophan wurde als Folge der Kräfte erklärt, die auf das Material während und nach der Koagulation und Regeneration einwirken. Dazu gehören die Viskositätskräfte der Behandlungsbäder, die innere Reibung beim Ziehen der Viskose ausserhalb der Presse, die Schrumpfungstendenzen des Films während der Bildung und Trocknung und die Spannungswirkung der Maschinenwalzen.

Received June 1, 1960