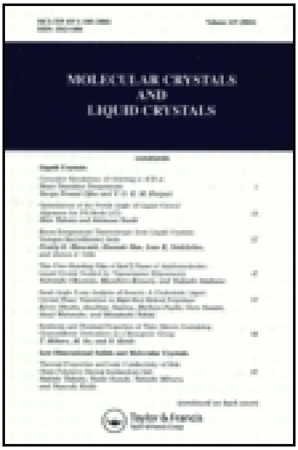

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

A Rheo-Optical Study of MBBA

H. Yanase [a] & T. Asada [a]
[a] Department of Polymer Chemistry, Kyoto University, Kyoto, 606, Japan
Version of record first published: 22 Sep 2006.

To cite this article: H. Yanase & T. Asada (1989): A Rheo-Optical Study of MBBA, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 167:1, 173-180

To link to this article: http://dx.doi.org/10.1080/00268948908037173

Mol. Cryst. Liq. Cryst., 1989, Vol. 167, pp. 173–180
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

A Rheo-Optical Study of MBBA

H. YANASE and T. ASADA
Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan

(*Received April 22, 1988; in final form June 21, 1988*)

A rheo-optical study has been performed on a low molecular weight nematic liquid crystal, MBBA, using a rheometer with cone and plate made of quartz. Both shear stress and transmitted light intensity of polarized and unpolarized light have been observed as a function of time after the onset of steady-shear to stationary state, and after cessation, as well as during steady shear flow. The transmitted light intensity varies with shear conditions, and shear stress also exhibits an unusual stepwise increase. These optical and mechanical results obtained can be interpreted in relation to the orientation of director, the generation and degeneration of disclinations and dynamic slip planes. It is also clear that some nuclei of disclinations can be excluded from the system having once experienced a shear deformation.

INTRODUCTION

A disclination is a discontinuity in orientation, *i.e.* a discontinuity in the director field $n(r)$. Disclination points (or lines) are seen in nematic liquid crystalline systems which are mobile and sometimes vanish easily by external excitation, such as shear or magnetic field. It is possible to observe the motion with a microscope directly. Samples as prepared in liquid crystalline states can not be free of disclinations unless special treatments should be carried out. A monodomain is not evident, but rather complicated polydomain textures are always observed. The textures in liquid crystals may also be deformed into others easily by external fields, such as electric, magnetic, and shear stress fields. As the structure of nematic textures is mainly governed by the nature of disclination points and lines, the process of the transformation from one texture to another must be closely correlated with the behavior of disclinations in the external fields. The mechanical and optical properties of a sample are also closely related to its texture, and thus it is important to investigate the dynamics of disclinations to know how to control the texture of a sample, *i.e.* the mechanical and optical properties of the materials.

Disclinations correspond to singularities in the orientation of the director field. Some kinds of disclinations were predicted theoretically by Frank,[1] based on his modified theory of the continuum theory for static nematic liquid crystals. The optical appearance and structures of disclinations have often been discussed in connection with his predictions. However, threadlike disclinations and line disclinations formed on shearing nematic liquid crystals, have been reported by several investigators.[2–3] It is known that there are two sorts of threads, thick and thin threads, according to Nehring's terminology.[4] Recently Graziano and Makcley made a detail study of the behavior of these threads in the steady-shear field with their apparatus which enables the microscopic observation of sheared samples between transparent discs.[5] Two types of disclinations were discussed in terms of the strength of disclinations.

The rheological behavior of such systems has already been investigated.[6–9] The flow curve reported so far can be generalized as follows: that is to say, the three-region flow curve proposed by Onogi and Asada[10]; apparent viscosity decreases with increasing shear rate at lower shear rate (Region I), apparent viscosity does not depend on shear rate at intermediate shear rate (Region II) and apparent viscosity decreases again with increasing shear rate at higher shear rate (Region III). Non-Newtonian flow with the shear thinning mentioned above has been observed. However, the interpretation of the flow curve, taking the inner structures into consideration, has not been accomplished.

In the current paper, a rheo-optical study has been conducted to clarify the change of the internal structure during flow. The orientation of director, the dynamic behavior of threads and other defects are investigated on low-molecular weight nematics, MBBA, in both the transient and the steady-shear fields, by the simultaneous observation of optical and mechanical properties.

EXPERIMENTAL

The typical sample of a low molecular weight nematic liquid crystal, N-(*p*-methoxybenzylidene)-*p*-buthylaniline (abbreviated MBBA hereafter) was obtained commercially from Sigma Chem. Co. and used without further purification. The sample is in nematic at room temperature (20°C–46°C). The polarized light method of rheo-optics described elsewhere[11] was adopted in the present study. The apparatus is composed of a cone-plate type rheometer and a series of optical systems. The cone and plate are made of quartz and 8.0 cm, 0.865 deg. in diameter and cone angle, respectively. A monochromatic light beam (λ = 632.8 nm) propagates along the axis of the cone-plate and goes through a polarizer, plate, sample (approximately 380 nm in thickness), cone and analyzer to be detected as transmitted light intensities by a photodetector.

Two optical quantities were measured; the transmitted light intensity of crossed polars in extinction position I_E (where the transmission axis of the polarizer coinciding with the flow direction)[11] and the transmitted light intensity of unpolarized light I_U. I_U was converted to turbidity in the text. In a series of the process from the start of steady-shear to the stationary state, and from the stationary state to the thermal equilibrium state after cessation of steady-shear, both optical quantities and shear stress were observed as a function of time at different shear rates at room temperature. At the same time microscopic observation was carried out.

Steady-Flow Behavior and Turbidity

The dependence on the steady-shear rate of steady-shear viscosity η (poise) (a) and turbidity (b) are shown in Figure 1. Viscosity decreases gradually with increasing the shear rate ($\dot{\gamma}$) up to ($\dot{\gamma}$) = 0.6 (sec^{-1}) and does not depend on the shear rate in the higher shear-rate region investigated. Region I and Region II (Newtonian region) are obviously seen in this sample within the shear rates examined and a measurement at higher shear rates will reveal the existence of Region III. The dependence of turbidity on the shear rate changes with shear-rate regions. In the lower shear rate region corresponding to Region I, turbidity is less dependent on the shear rate, but in the higher shear rate region corresponding to Region II, it increases linearly with increasing shear rate. The dependence of I_E on shear rate was almost the same as that of turbidity and it was not possible to detect a variation of birefringence.

According to microscopic observation, on the lower shear rate side of Region I, distinct threads which float in continuous matrix and are extended in flow direction and at the same time their number also increases on the higher shear rate side of Region I. Near the boundary between Region I and Region II, wholly extended threads can no longer hold their structures, causing them to vanish into matrix. Then, the matrix is divided into tiny domains. The contour of the domains seems to twinkle between crossed polarizers and each domain moves independently. The appearance is analogous to that of the dynamic scattering mode of MBBA in electric fields under certain definite conditions.[12]

The boundary of each domain may be a slip plane which can propagate easily through the liquid crystalline matrix. The trajectory of the slip plane can be ob-

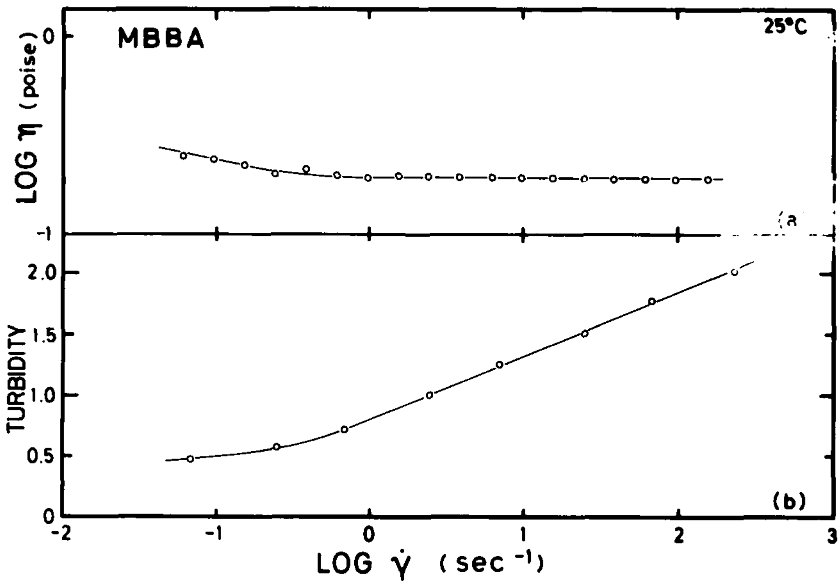

FIGURE 1 (a) The dependence of apparent viscosity η of MBBA on shear rate $\dot{\gamma}$ at 25°C. (b) The dependence of turbidity on shear rate.

served as transient twinkles with a microscope between crossed polarizers or in natural light. Therefore, turbidity in Region II may be regarded as a measure of both mobility and number of the dynamic slip plane. That the linear relationship between turbidity and shear rate holds in Region II means that the mobility and numbers of dynamic slip plane per unit volume increase with increasing shear rate, while apparent viscosity remains constant. It is interesting that the generation of the dynamic slip plane cannot affect the bulk properties of apparent viscosity, so that the mobility of the slip plane is considered to be much higher once it is formed.

Over the shear rate region examined, the variation of retardation was not observed and both turbidity and I_E behaved alike against the shear rate. Consequently the directors in the liquid crystalline state of MBBA did not orient in the flow direction in steady-shear field, being quite different from those of polymer liquid crystals for which directors orient in flow direction with increasing shear rate.[10] It is concluded that threads and other dynamic defects, called dynamic slip planes, rule the structures of the present system in the shear field and the flow manner is not in laminar but considerably disturbed with respect to the director orientation.

Transient Behavior of Stress and Optical Quantities

The transient behavior after onset and after cessation of steady-shear flow will be described. In Figure 2 the variation of turbidity is shown as a function of time after the onset of steady-shear at different shear rates. At any shear rate turbidity decreases with time during the early stage and then becomes minimum, followed by a steep increase to the stationary value, which is shown in Figure 1 (b) as a function of shear rate. The result obtained with a virgin sample is that of $\dot{\gamma}$ = 0.694 (sec^{-1}). Others were obtained successively with the sample which experienced a shear deformation at a lower shear rate. The values of turbidity in the quiescent state (indicated by the circles in parentheses in the Figure) are lower as the shear

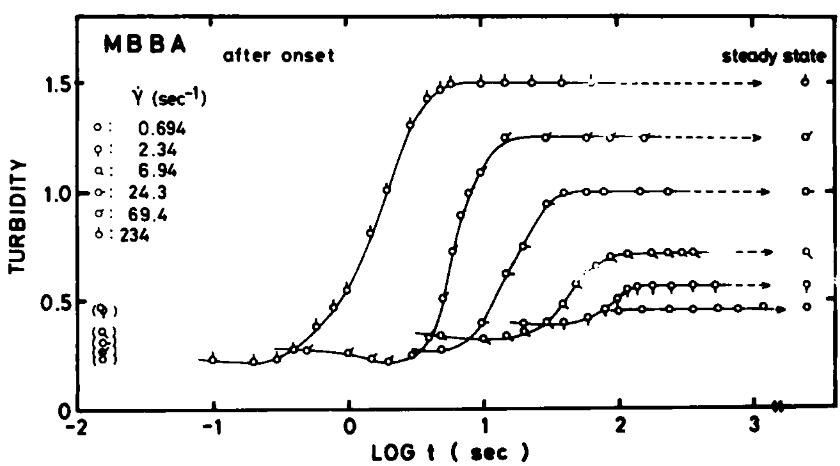

FIGURE 2 The variation of turbidity with time (on logarithmic scale) after onset of steady-shear flow at different shear rates.

rate experienced by a sample becomes higher, *i.e.* a sample having once experienced shear flow is more transparent than a virgin sample, and the higher the shear rate, the more transparent a sample becomes. This result suggests that the nuclei of disclinations can be excluded from the system by shearing. The time required for the stationary state to be reached after onset of steady-shear depends on the shear rate. The lower the shear rate, the longer the time required.

From microscopic observation, the textures vary with time after onset of steady-shear flow. As an example, the results obtained by the case of $\dot{\gamma} = 24.3$ (sec^{-1}) belonging to Region II is reviewed. There are no threads but the sample is somewhat turbid even at rest. About 7 sec after the onset of steady-shear, when turbidity becomes minimum, the director oriented in the flow direction because the whole field of vision became uniform in a moment and then disclination lines appeared. Finally, tiny domains with dynamic slip planes came to be dominant in succession.

Mechanical properties have been studied, focusing especially on the transient phenomena after the onset of steady-shear. Anomalous behavior has been found within certain shear rate regions. The stress growth in stepwise manner with time after the onset of steady-shear and then stress overshoot was observed, as shown in Figure 3, at different shear rates. Stepwise stress growth was also observed by Osaki *et al.*[13] in other systems of block copolymers. The ordinate represents the relative stress σ/σ_{st} in percent, where σ and σ_{st} are the stress at time t, and the stress during steady-shear flow, respectively. As an example, the most characteristic curve of stress growth obtained by the case of $\dot{\gamma} = 20.8$ (sec^{-1}) is illustrated. The curve is composed of two portions, *i.e.* a portion of the shoulder immediate after

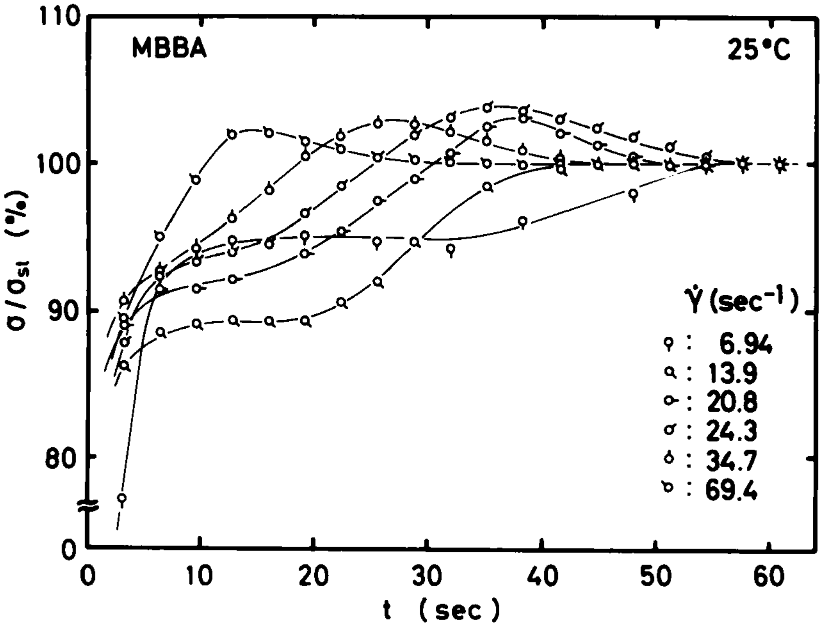

FIGURE 3 The variation of relative stress σ/σ_{st} with time (on linear scale) after onset of steady-shear flow at different shear rates, where σ and σ_{st} are shear stress at t and during steady flow, respectively.

the start of steady-shear and a portion of stress overshoot after a longer time. At shear rates lower than the shear rate (20.8 sec^{-1}), stress overshoot was not observed. For shear rates higher than the shear rate, a portion of shoulder becomes narrower with increasing shear rate.

Figure 4 shows the dependence of relative stress σ/σ_{st} on strain γ ($= \dot{\gamma} \cdot t$) at different shear rates. As is evident from the Figure, both a portion of the shoulders and a portion of the stress overshoots are located in almost the same strain region. Therefore, it is concluded that the deformation mechanisms of the liquid crystalline system by steady-shear is determined by the strain.

The optical data shown in Figure 2 corresponding to the shear rate region (from 6.94 to 69.4 sec^{-1}) are shown in Figure 5. In the Figure the dependence of turbidity on strain at different shear rates is presented in the same scales as those of Figure 4. From this Figure, the same tendency is recognized, *i.e.* the characteristic features are understood systematically by strain as in the case of stress growth. Comparing Figure 5 with Figure 4, it is clear that the strain at which the turbidity becomes minimum coincides approximately with that at a portion of the shoulder. The coincidence suggests that a portion of the shoulder in the stress growth curve should be connected with the alignment of directors in flow direction.

In Figure 6 the variation of turbidity with time after cessation of steady-shear flow is shown at different shear rates. The stress relaxation was also measured simultaneously but it could not be actually measured, because the relaxation time was too short to be detected. Therefore only the optical data will be discussed. The higher the shear rates during steady-shear flow, the faster the turbidity decreases. The differential quantity of turbidity, during steady-shear flow and at rest,

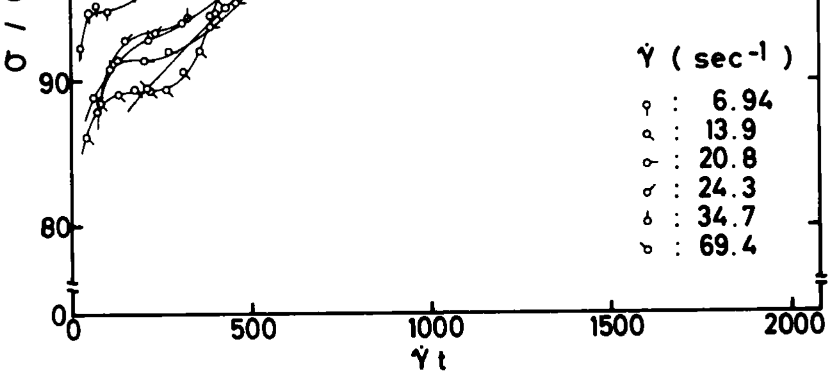

FIGURE 4 The variation of relative stress σ/σ_{st} with strain ($\dot{\gamma} \cdot t$) after onset of steady-shear flow at different shear rates.

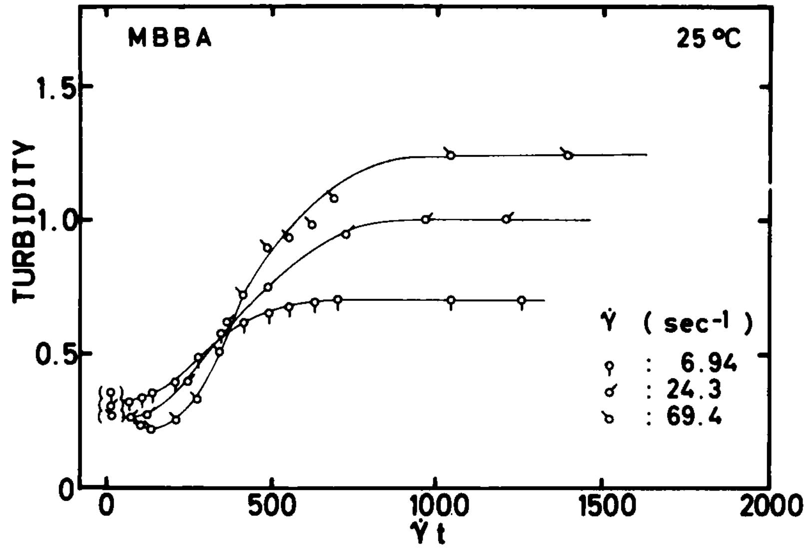

FIGURE 5 The variation of turbidity with strain after onset of steady-shear flow at different shear rates.

is very dependent on shear rate, *i.e.* the faster the shear rate, the larger the difference. At shear rate, 0.694 (sec^{-1}) belonging to Region I, the difference was not observed and neither were the threads. Using microscopic observation threads begin to be detected during steady-shear flow at 2.34 (sec^{-1}). The threads prolonged in flow direction by shear stress during flow, and then they shrinked to circles, the diameters of which reduced to points meanwhile and they finally disappeared after longer time.

It was possible to trace the process of relaxation and fading out in disclinations (threads) by the observation of turbidity as shown in the Figure. However, at the shear rates in Region II, tiny domains with dynamic slip planes were vividly ob-

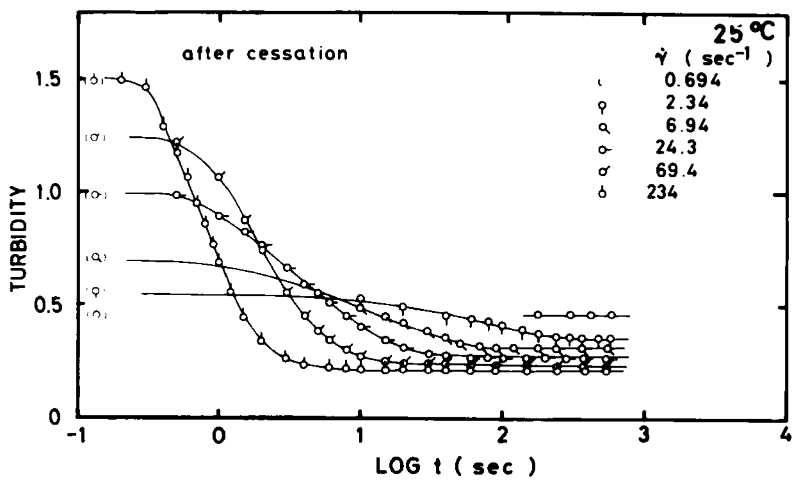

FIGURE 6 The variation of turbidity with time (on logarithmic scale) after cessation of steady-shear flow at different shear rates.

served during flow as mentioned above. When the turbidity decreased drastically in a short time after cessation of steady-shear ($\dot{\gamma}$ = 69.4, 234 sec^{-1}), the tiny domains were transformed into a somewhat turbid phase at rest, while the appearance of threads and their relaxation were observed after a longer time in the case of $\dot{\gamma}$ = 6.94, 24.3 (sec^{-1}). According to the results, it is certain that there are two kinds of defects during flow, dynamic slip planes which separate tiny domains, and threads. The former disappears during the early stage, while the latter relaxes and disappears in further time after cessation of steady-shear flow, at the rates related reciprocally to the previous shear rates.

Flow and Deformation Mechanisms of MBBA

During steady-shear flow of MBBA in the liquid crystalline state, there are two different kinds of flow mechanisms. One is the flow of liquid crystalline matrix as a whole, or the matrix with extended disclination lines (threads) floating in the matrix as a whole, and the other is the flow of tiny domains with rapid change of slip plane. It is clear that each flow occurs in a definite shear rate region, *i.e.* Region I and Region II, respectively. The transient process from the rest to the stationary state after the onset of steady-shear flow was understood in terms of the variation of textures, the alignment of director fields, and the generation of threads and tiny domains with dynamic slip plane, based on the optical and mechanical data.

Stepwise stress growth composed of a portion of the shoulder and a portion of stress overshoot was found in a certain shear-rate region. The portion of the shoulder may be concerned with the alignment of directors in flow direction. There are two kinds of defects during flow, dynamic slip plane between tiny domains, and threads. The relaxation and disappearance of them after cessation of steady-shear were traced through the variation of turbidity with time. The dynamic defects disappear at first and then the threads appear and reduce. The rate of relaxation and disappearance is found to be related reciprocally to the previous shear rate. Since dynamic defects can not be distinguished from threads only by the measurements of turbidity, systematic studies on the time constant of the decreasing curve (in Figure 6) will present the pertinent information.

References

1. F. C. Frank, *Faraday Discuss. Chem. Soc.*, **25**, 19 (1958).
2. P. E. Cladis and S. Torza, *Phys. Rev. Lett.*, **35**, 1283 (1975).
3. J. Wahl and F. Fischer, *Mol. Cryst. Liq. Cryst.*, **22**, 59 (1973).
4. J. Nehring, *Phys. Rev.*, **A7**, 1737 (1973).
5. D. J. Graziano and M. R. Mackley, *Mol. Cryst. Liq. Cryst.*, **106**, 103 (1984).
6. R. S. Porter and J. F. Johnson, *J. Appl. Phys.*, **34**, 51 (1963).
7. R. S. Porter and J. F. Johnson, *ibid.*, **34**, 55 (1963).
8. J. Fisher and A. G. Fredrickson, *Mol. Cryst. Liq. Cryst.*, **8**, 267 (1969).
9. T. Asada and S. Onogi, *Polym. Eng. Rev.*, **3**, 323 (1983).
10. S. Onogi and T. Asada, *Rheology* (Plenum Press, New York, 1980), ed. by G. Astarita, G. Marrucci and L. Nicolais, vol. 1, pp. 127–147.
11. T. Asada *et al.*, *Macromolecules*, **13**, 867 (1980).
12. G. Heilmeyer, L. A. Zanoni and L. Barton, *Proc. Inst. Elect. Electron. Engrs.*, **56**, 1162 (1968).
13. K. Osaki, *et al.*, *Polym. J.*, **11**, 33 (1979).