

Thermo-Optical and Differential Scanning Calorimetric Observations of Mobility Transitions in Polystyrene-Poly(2,6-Dimethyl-1,4- Phenylene Oxide) Blends

A. R. SHULTZ AND B. M. GENDRON, *Polymer Chemistry Branch,
Chemical Laboratory, General Electric Corporate Research and Development,
Schenectady, New York 12301*

Synopsis

Transition temperatures by thermo-optical analysis (TOA) and by DSC were measured on films of polystyrene (PS), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO resin) and nine homogeneous blends of these polymers. The TOA procedure consists of automatically monitoring light transmission through birefringent scratches in a film during heating at constant rate in a microscope hot stage between crossed (90°) plane polarizers. The T_{TOA} transition temperature, defined as the temperature of birefringence disappearance in the scratches, increased monotonically from 113°C for pure PS to 222°C for pure PPO resin at a 10°/min heating rate. The T_g (DSC) similarly ranged from 99°C to 212°C at a 20°/min heating rate. The TOA technique as described should be a useful addition to thermomechanical studies of transparent polymers and polymer blends.

INTRODUCTION

Glass transitions, ductile-brittle transitions, and other phenomena associated with changes in polymer mobility have been investigated by many techniques. During the past year it was discovered by Kovacs and Hobbs¹ that polarizing microscopic observation of the disappearance of scratch-induced birefringence in glassy or semicrystalline polymers during heating is a convenient means of detecting the onset of greatly increased segmental mobility in polymer films. The present study examines by this technique the disappearance of birefringence in homogeneous blends of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO resin, registered trademark of the General Electric Company) during 10°/min heating. The thermo-optical transition temperatures T_{TOA} thus obtained will be compared with the specific heat transition temperatures T_g (DSC), obtained by differential scanning calorimetry at a 20°/min heating rate.

Blends of polystyrene and PPO resins were recognized several years ago as being homogeneous at all compositions.² True thermodynamic miscibility of these two polymers in ternary solutions with toluene further attests to

their compatibility.³ Differential scanning-calorimetric⁴ and adiabatic-calorimetric^{5,6} studies of PPO resins have shown their glass transitions at rather slow heating rates to be about 207°C. Many measurements of T_g (DSC) have been made on PS-PPO resin blends during the past eight years, with two published accounts appearing in 1970.^{7,8} A monotonic increase in T_g (DSC) with increasing PPO resin content is observed in accord with expectation for compatible blends.

No studies have been reported on the stress-optical or strain-optical birefringence characteristics of PPO resins. On the other hand, a wealth of experimental and theoretical publications exists concerning these characteristics for PS. Birefringence studies have been reported on styrene atactic homopolymers,⁹⁻⁶⁹ isotactic homopolymers,⁶⁰⁻⁶² statistical copolymers,⁶³⁻⁶⁶ block copolymers,⁶⁷⁻⁶⁹ graft copolymers,⁷⁰ statistical terpolymers,⁷¹⁻⁷³ and crosslinked networks.⁷⁴⁻⁷⁹ Birefringence has been used to observe residual orientation effects in PS resulting from specific processing conditions.⁵⁴⁻⁵⁹ Most of the birefringence investigations have been concerned with stressed films and sheets, but work has also been performed on filaments⁴⁵⁻⁵³ and on spheres⁷⁴ internally stressed by swelling. The stress-optical coefficient for PS at low strains is positive at temperatures well below T_g , while at high strains near and above T_g it is negative. This negative contribution arises from the polarizability of the phenyl groups perpendicular to the orientation direction of the somewhat stretched-out chains.^{9,41,46,80,81} In the present study, the sign or absolute magnitude of the birefringence is not determined. It is merely necessary that the temperature of essential disappearance of birefringence in the scratches is not made ambiguous by any of several stress-optical or strain-optical artifacts.¹

Several annealing^{23,27,30,54,59,61} and multitemperature^{18,19,33-38,51,65,66,72,75} observations of birefringence changes in stressed and strained PS have been made. The observations of birefringence change to detect glass transitions by experiments involving temperature steps⁶¹ or constant rate temperature scans (at 0.5°/min^{18,19} and 1.0°/min^{37,38}) are especially pertinent to the present study. Our technique differs principally in the introduction of birefringence by scratching well below the T_g of the polymer films and in the observation of polarized light transmission due to birefringence effects rather than measurement of the birefringence itself. Also, the present work is the first study of stress/strain-optical transition temperatures in homogeneous polymer blends.

EXPERIMENTAL

Materials and Sample Preparations

Polystyrene Lot 4a (Pressure Chemical Company), an anionically polymerized polymer of molecular weight 97,200 and a quoted $M_w/M_n > 1.06$ was used. The PPO resin, designated PR5255, has an intrinsic viscosity at 30°C in chloroform of 0.49 dl/g, $M_n = 18,500$ by osmotic pressure, and

$M_w = 37,200$ by light scattering. The PS and PPO resin will occasionally be referred to as component 1 and component 2, respectively.

Initially films were cast by doctor blade onto Mylar sheet from solutions containing 5.0 g PS-PPO resin and 25 ml toluene at 0.1 weight fraction composition intervals. Rapid air drying of these films produced "orange peel" surface textures, and films containing weight fraction PPO resin (w_2) ≥ 0.60 were opaque due to the PPO resin crystallization during drying. Some preliminary thermo-optical analysis (TOA) measurements, not reported, were made on small portions of these films, but the major portion of each was redissolved in 40 ml toluene at 60°C. A drop of each of these solutions was cast on a microscope slide and air dried. These air-dried films were annealed on the slides at 270°C for 3 min and then quenched to room temperature to give clear, amorphous samples. These films on the microscope slides are designated SM-1 to SM-11. The remaining solutions were precipitated into 200 ml methanol in a Waring blender. The precipitated blends were dried under vacuum for 1/2 hr at room temperature and for 20 hr at 80°C. The dry powders were compression molded between aluminum sheets for 2 min at temperatures ranging from 180°C for pure PS resin to 270°C for pure PPO resin, followed by quenching in water at room temperature. The clear, transparent films ranged in thickness from 5 to 8 mils. These films are designated PM-1 to PM-11.

Apparatus and Experimental Procedure

DSC measurements were made with a Perkin-Elmer differential scanning calorimeter Model DSC-1B. Sample weights were approximately 10 mg. The heating rate was 20°/min, and temperature calibration was accomplished with naphthalene, benzoic acid, indium, tin, bismuth, lead, and zinc as standards. A nitrogen flow of 0.04 sefg was maintained through the chamber around the sealed aluminum sample containers. DSC traces were taken twice for each sample over the range of 45° to 280°C. Between the first and second heating, the sample was cooled rapidly by removing its container from the 280°C stage and placing it on a metal surface at room temperature.

The thermo-optical transition temperatures T_{TOA} were determined with the thermo-optical analyzer (TOA), which is schematically represented in Figure 1. It consists of a triocular polarizing microscope M (Zeiss standard WL) equipped with a hot stage H (Mettler FP21) programmed by a control

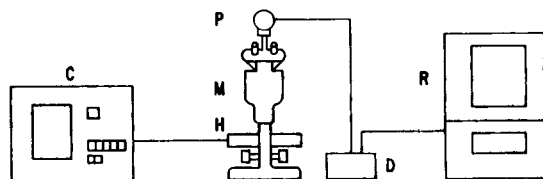


Fig. 1. Schematic representation of thermo-optical analysis apparatus: C, temperature programmer; H, hot stage; M, polarizing microscope; P, photocell; D, voltage divider; R, strip chart recorder.

unit C (Mettler FP2) and a photocell P receiving transmitted light. The photocurrent is fed to a voltage divider D, whose output is displayed on a strip chart recorder R (Leeds and Northrup, AZAR, Speedomax) against a time base.

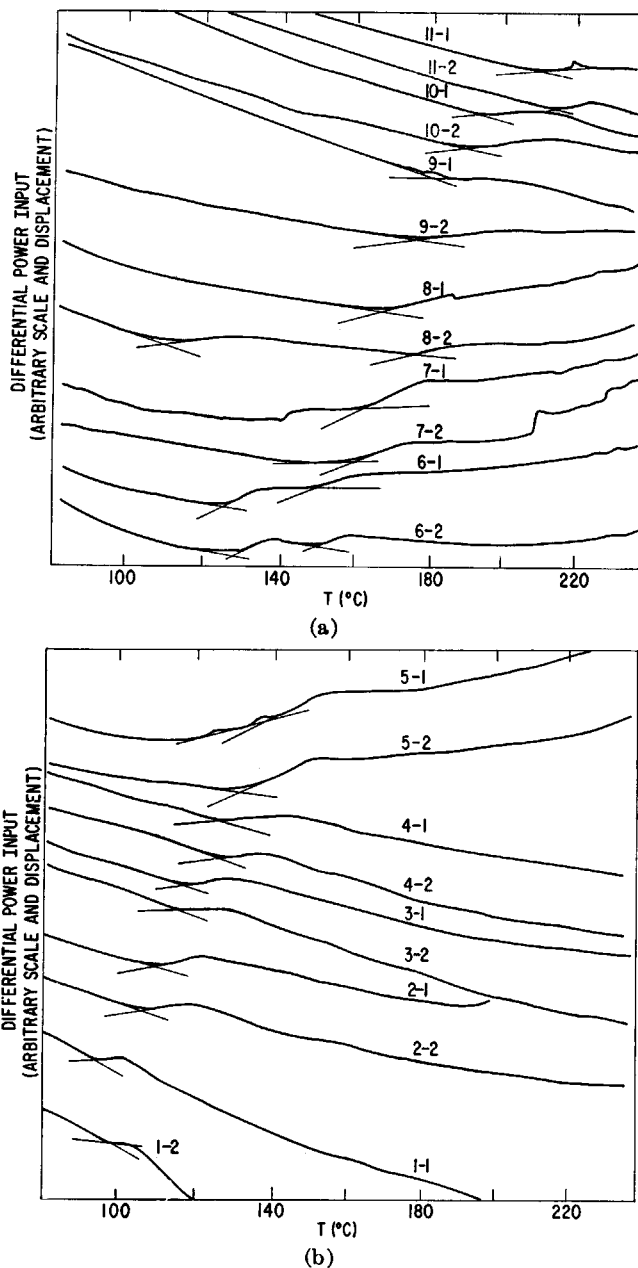


Fig. 2. DSC traces of differential power input vs. temperature for the 11 PS-PPO resin blend film samples. Heating rate 20°C/min.

The experimental procedure involves scribing by hand close-spaced scratches into the polymer film surface with a steel stylus at room temperature and placing the film on its slide in the microscope hot stage between crossed (90°) plane polarizer and analyzer. White light from an incandescent tungsten bulb is used. Light is transmitted to the photocell only through the birefringent scratches. The microscope aperture, voltage divider, and recorder range are arbitrarily set to give a nearly full-scale voltage reading on the strip chart. With the stage initially stabilized at 60°C , the temperature rise controller ($10^\circ/\text{min}$) and the chart drive ($1/3$ in./min) are simultaneously started. The strip chart record is then essentially a plot of transmitted light intensity versus sample temperature ($30^\circ/\text{in.}$ in the temperature axis). At some temperature, the molecular motions in the sample become sufficiently rapid to allow relaxation of the stress/strain-induced birefringence, and the transmitted light intensity rapidly diminishes to a near-zero value. The intersection of the tangent to the light intensity-temperature curve at its inflection point with the tangent to the subsequent low-slope or zero-slope baseline locates T_{TOA} . The temperature readings on the controller were calibrated at a $10^\circ/\text{min}$ heating rate with naphthalene (triple point 80.24°C), adipic acid (triple point 151.46°C), and 2-chloroanthraquinone (triple point 208.95°C) standards. Their apparent melting points in the TOA using the crossed polarizer-analyzer arrangement were 81.9° , 154.1° , and 211.3°C , respectively. Therefore, 2°C was subtracted from each apparent (controller dial) T_{TOA} to yield the reported T_{TOA} .

RESULTS AND DISCUSSION

The DSC traces ($20^\circ/\text{min}$) for the pressed PS-PPO resin blends PM-1 to PM-11 are shown in Figures 2a and 2b. The second number in the labels indicates first or second run. Although the curves are not completely unambiguous with regard to the specific heat transition locations, especially in the middle mixture composition region, fairly well-defined $T_g(\text{DSC})$ values are obtained and listed in Table I.

Figure 3 presents representative TOA curves for the PM-1 to PM-11 pressed films. The vertical scale, labeled transmitted light intensity although actually a voltage reading from the photoelectric circuit, is arbitrary, and the vertical displacement of the curves for display clarity is also arbitrary. The T_{TOA} values from these curves and from other runs involving rescratching of run-and-quenched samples or new scratched samples are listed in Table I. Also in Table I are listed T_{TOA} values for the toluene-cast and annealed films SM-1 to SM-11.

The T_{TOA} and $T_g(\text{DSC})$ of the PS-PPO resin blends are plotted against composition in Figure 4. The T_{TOA} -versus- w_2 plot is a smooth curve showing very little scatter, with the exception of the pure PS and the $w_2 = 0.2$ data points. The $T_g(\text{DSC})$ -versus- w_2 plot is a smooth curve up to about $w_2 = 0.5$, beyond which greater scatter occurs. The data are fit extremely well by the relations

TABLE I
DSC and TOA Data for Films of
Polystyrene-Poly(2,6-dimethyl-1,4-phenylene Oxide) Mixtures

Wt. fraction PPO resin	PM series	$T_g(\text{DSC}), ^\circ\text{C}$		$T_{\text{TOA}}, ^\circ\text{C}$	SM series	$T_{\text{TOA}}, ^\circ\text{C}$
0.000	1	91	99	110, 116(95)	1	(116), 110
0.100	2	109	107	120, 120, 119, 119	2	118, 119
0.200	3	118	117	125, 125, 124, 124	3	124, 124
0.300	4	127	127	141, 141, 140, 140	4	144, 145
0.400	5	139	129	151, 151, 150, 150, 149, 149	5	150, 158, 158
0.500	6	151(127)	152(129)	161, 160, 160, 159	6	165, 170
0.600	7	165	161	172, 171, 171, 171	7	162, 175
0.700	8	176(173)	176(112)	185, 183, 183, 182	8	190, 188
9.800	9	184	177	196, 196, 195, 195	9	191, 193
0.900	10	194	192	211, 210, 209, 209	10	206, 207
1.000	11	211	213	223, 222, 222, 221	11	222, 222

$$1/T_{\text{TOA}} = (1 - w_2)/386.2 + w_2/495.2 \quad (1)$$

$$1/T_g(\text{DSC}) = (1 - w_2)/372.2 + w_2/485.2 \quad (2)$$

with temperatures in degrees Kelvin. The curves drawn in Figure 4 correspond to these equations.

The data were also fitted by least-squares linear regression to the relation

$$T(\text{transition}) = A + Bw_2 + Cw_2(1 - w_2). \quad (3)$$

with $T(\text{transition})$ in $^\circ\text{C}$, the constants in eq. (3) for T_{TOA} are $A = 112.1$, $B = 110.2$, and $C = -27.17$, with an index of determination (40 data points) of 0.9987. For $T_g(\text{DSC})$, the constants are $A = 98.2$, $B = 111.2$, and $C = -18.80$, with an index of determination (21 data points) of 0.9899.

The present use of stress/strain-optical measurement to detect a chain-mobility transition temperature relies upon a rather complex set of mechanical and optical parameters. Scratching the glassy polymer blends produces both local stress-optical and slightly longer range strain-optical birefringence. The high, but not measured, stress/strain-optical coefficients of PS and PPO resin make this system very convenient for these measurements. Refraction of light in the near-surface layers of the plastic and at the plastic-air interface of the scratches produces an ill-

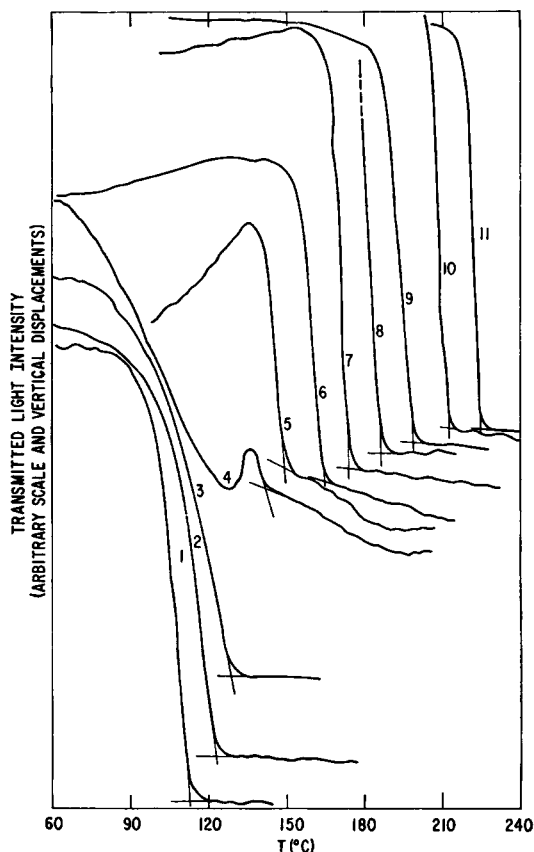


Fig. 3. Thermo-optical curves of transmitted light intensity vs. temperature for the 11 PS-PPO resin blend films. Heating rate $10^{\circ}\text{C}/\text{min}$.

defined optical geometry. Chromatic dispersion of the birefringence and wedge interference effects often cause the white light transmission to pass through several orders of interference colors during heating just prior to the final zero-order fadeout. Lack of linearity in photocell response due to wavelength and polarization variations can affect photocurrent output in this region. Despite the complex features of the TOA measurement, a remarkably reproducible T_{TOA} is obtained in this system. The same T_{TOA} is found on different film specimens of the same blend composition, on different scratch patterns and scratching conditions, and on first, second, and third temperature scans of a given sample with interspersed scribing.

The T_{TOA} and T_g (DSC) curves are nearly parallel, differing by 14°C at the pure PS and by 10°C at the pure PPO resin end. It is obvious that there is a close correlation between the onset of chain motions responsible for the specific heat increase and those responsible for stress/strain-optical relaxation. The actual correspondence of the two phenomena is much

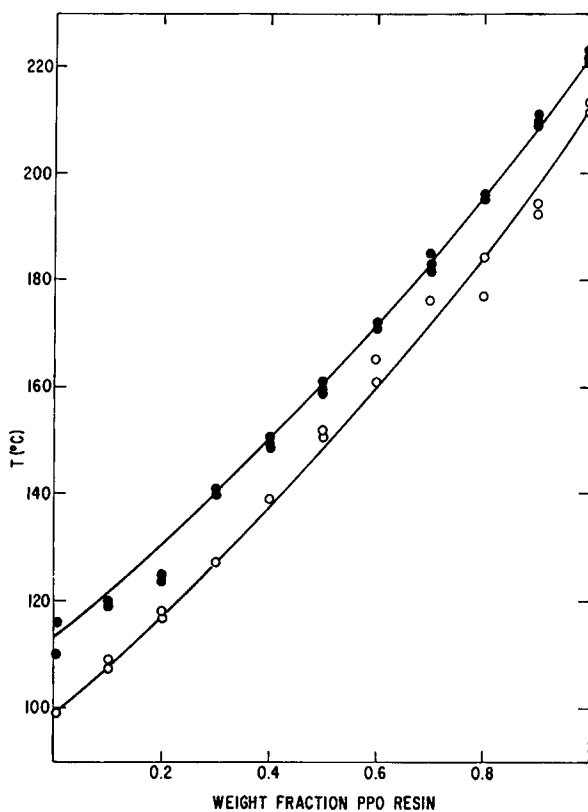


Fig. 4. Thermo-optical transition temperatures and glass transition temperatures by DSC as function of PS-PPO resin blend compositions: (●) T_{TOA} (○) T_g (DSC).

closer than indicated, since T_g (DSC) is taken as the temperature at which the specific heat increase appears to start in the scan, while the T_{TOA} is here taken as the temperature in the scan at which light transmission has dropped to a low, limiting value. Considerable optical changes proceed in the scratches in the 10° – 15°C region below T_{TOA} as here defined. The sharpness and reproducibility of the “endpoint” temperature of the transition recommend it as the definition of T_{TOA} . Use of the inflection point in the (decreasing) transmitted light intensity-versus-temperature curve to define the transition temperature in a manner comparable to the use of the inflection point in birefringence-versus-temperature curves^{18,19} under constant tensile load is conceivable. However, in the latter “constant stress” experiments, the change (increase) in birefringence due to the onset of strain orientation was load sensitive, and the inflection point temperature increased with decreasing load. Our TOA measurements are more comparable to the recently reported free stress/strain relaxation technique³⁷; and, indeed, our T_{TOA} value for polystyrene lies about midway in the T_0 (100°) to T_1 (120°) transition region of that study. The negative birefringence induced by tensile strain orientation at T_e (110°) $>$ T_g in

polystyrene³⁴ certainly must differ considerably in polymer chain conformation origin from that of the stress/strain-induced birefringence within our scratch marks introduced at T (30°) $< T_g$. In spite of this, the disappearance of birefringence occurs in the same temperature region in both experiments.

Thermo-optical analyses of scratched PS-PPO resin blend films by means of an automatic-recording polarized light transmission-temperature scan technique have revealed sharp, reproducible transition temperatures T_{TOA} that parallel T_g (DSC). The present TOA technique should be a valuable addition to physical property studies on transparent polymers and their blends.

The authors wish to thank Prof. A. Kovacs and Dr. S. Y. Hobbs for drawing their attention to the TOA technique possibilities and for assembly of the TOA apparatus. The consultation of Dr. D. G. LeGrand concerning various rheo-optical effects which may enter into data interpretation is also acknowledged.

References

1. A. Kovacs and S. Y. Hobbs, *J. Appl. Polym. Sci.*, **16**, 301(1972).
2. E. P. Cizek (to the General Electric Company) U.S. Pat. 3,383,435 (May 14, 1968).
3. A. R. Shultz and C. R. McCullough, *J. Polym. Sci. A-2*, **10**, 307 (1972).
4. F. E. Karasz and J. M. O'Reilly, *J. Polym. Sci. B*, **3**, 561 (1965).
5. F. E. Karasz, J. M. O'Reilly, H. E. Bair, and R. A. Kluge, *ACS Polymer Preprints*, **9**, 822 (1968).
6. F. E. Karasz, H. E. Bair, and J. M. O'Reilly, *J. Polym. Sci. A-2*, **6**, 1141 (1968).
7. J. Stoelting, F. E. Karasz, and W. J. McKnight, *Polym. Sci. Eng.*, **10**, 133 (1970).
8. H. E. Bair, *Polym. Sci. and Eng.*, **10**, 247 (1970).
9. Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, **3**, 294 (1970).
10. R. D. Andrews and J. F. Rudd, *Bull. Amer. Phys. Soc. (2)*, **2**, 148 (1957).
11. R. D. Andrews and T. J. Hammack, *J. Polym. Sci. C*, **5**, 101 (1964).
12. S. Bagavantam and Y. Krishna Murty, *Proc. Indian Acad. Sci.*, **43A**, 203 (1956); *C.A.*, **50**, 13499d.
13. N. M. Bazhenov, M. V. Vol'kenstein, Yu. Ya. Gotlib, and L. D. Rozenshtein, *Zhur. Tekh. Fiz.*, **26**, 1730 (1956); *C.A.*, **51**, 1695c.
14. A. D. Gabaraeva, M. F. Milagin, and N. I. Shishkin, *Mekh. Polim. (6)*, 1105 (1965); *C.A.*, **69**, 10902j.
15. E. F. Gurnee, L. T. Patterson, and R. D. Andrews, *J. Appl. Phys.*, **26**, 1106 (1955).
16. E. F. Gurnee, *J. Polym. Sci. A-2*, **5**, 817 (1967).
17. J. Joussot-Dubien, *J. Chim. Phys.*, **56**, 513 (1959).
18. M. Kaneko, R. Murai, K. Kishi, and D. Mori, *J. Fac. Sci. Hokkaido Univ., Ser II*, **4**, 305 (1954); *C.A.*, **49**, 16511f.
19. M. Kaneko, R. Murai, K. Kishi, and D. Mori, *J. Phys. Soc. Japan*, **10**, 78 (1955).
20. H. Kolsky and A. C. Shearman, *Proc. Phys. Soc. (London)*, **55**, 383 (1943).
21. R. Kubo, *J. Phys. Soc. Japan*, **2**, 47, 51, 84 (1947).
22. R. Kubo, *J. Colloid Sci.*, **2**, 527 (1947).
23. L. A. Laius and E. V. Kuvshinskii, *Mekh. Polim., Akad. Nauk Latv. SSR (2)*, 163 (1966); *C.A.*, **65**, 9040h.
24. L. A. Laius and E. V. Kuvshinskii, *ibid.*, (3), 435 (1966); *C.A.*, **65**, 15605e.
25. J. Majer and J. Dvorak, *Kunststoff-Rundschauf*, **4**, 345 (1957); *C.A.*, **52**, 21214h.
26. M. F. Milagin, A. D. Gabaraeva, and N. I. Shishkin, *Fiz. Tverd. Tela*, **6** (12), 3636 (1964); *C.A.*, **62**, 6582c.

27. M. F. Milagin, N. I. Shishkin, and A. D. Gabaraeva, *ibid.*, **6** (5), 1413 (1964); *C.A.*, **60**, 7181e.
28. M. F. Milagin, A. D. Gabaraeva, and N. I. Shishkin, *Vysokomol. Soedin., Ser. A.*, **12** (3), 513 (1970); *C.A.*, **73**, 4321k.
29. L. E. Nielsen and R. Buchdahl, *J. Chem. Phys.*, **17**, 839 (1949).
30. L. E. Nielsen and R. Buchdahl, *J. Appl. Phys.*, **21**, 488 (1950).
31. L. E. Nielsen and R. Buchdahl, *J. Colloid Sci.*, **5**, 282 (1950).
32. B. Persoz and J. Bonnet, *Cahier Groupe Franc. Etudes Rheol.*, **1** (No. 2), 6 (1956); *C.A.*, **53**, 758f.
33. B. Persoz, G. Grenier, and J. Bonnet, *ibid.*, **5** (Nos. 1-4), 253 (1960); *C.A.*, **57**, 8718f.
34. J. F. Rudd and E. F. Gurnee, *Bull. Amer. Phys. Soc.* (2), **2**, 148 (1957).
35. J. F. Rudd and E. F. Gurnee, *J. Polym. Sci. A*, **1**, 2857 (1963).
36. J. F. Rudd, *J. Polym. Sci. B*, **3**, 345 (1965).
37. A. I. Sheyanova, S. I. Sokolov, and N. A. Shchegolevskaya, *Dokl. Akad. Nauk SSSR*, **172** (2), 397 (1967); *C.A.*, **66**, 55905s.
38. A. I. Sheyanova, S. I. Sokolov, and N. A. Shchegolevskaya, *Mekh. Polim.*, (6), 1110 (1967); *C.A.*, **69**, 10900g.
39. N. I. Shishkin, M. F. Milagin, and A. D. Gabaraeva, *Fiz. Tverd. Tela*, **5**, 3453 (1963); *C.A.*, **60**, 8150b.
40. R. S. Stein, *J. Polym. Sci.*, **24**, 383 (1957).
41. R. S. Stein, *J. Appl. Phys.*, **32**, 1280 (1961).
42. O. N. Trapeznikova, *J. Phys. Chem. (USSR)*, **22**, 395 (1948); *C.A.*, **42**, 57744f.
43. O. N. Trapeznikova and E. I. Feofanova, *Zhur. Fiz. Khim.*, **35**, 1114 (1961); *C.A.*, **55**, 26514g.
44. A. Winaver, *Compt. Rend.*, **238**, 463, 1810 (1954).
45. R. D. Andrews, Jr., *J. Appl. Phys.*, **25**, 1223 (1954).
46. E. F. Gurnee, *ibid.*, **25**, 1232 (1954).
47. R. D. Andrews, Jr., and J. F. Rudd, *ibid.*, **27**, 990 (1956).
48. J. F. Rudd and R. D. Andrews, Jr., *ibid.*, **27**, 996 (1956).
49. J. F. Rudd and R. D. Andrews, Jr., *ibid.*, **29**, 1421 (1958).
50. K. Heckel, *Z. Angew. Phys.*, **7**, 291 (1955); *C.A.*, **49**, 14375a.
51. R. P. Sheldon, *J. Appl. Polym. Sci.*, **6**, S43 (1962).
52. J. L. Williams, K. J. Cleereman, H. J. Karam, and H. W. Rinn, *J. Polym. Sci.*, **8**, 345 (1952).
53. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **6**, 361 (1962).
54. N. M. Dashko and E. A. Sporyagin, *Plast. Massy*, (10), 62 (1969); *C.A.*, **72**, 56160f.
55. T. H. Farrell, R. E. Kugler, and D. I. Mayne (to Eastman Kodak Co.), U.S. Pat. 2,816,027 (Dec. 10, 1957).
56. M. Inoue, H. Yamada, T. Fukami, and M. Takagi, *Kobunshi Kagaku*, **22** (237), 17 (1965).
57. G. B. Jackson and R. L. Ballman, *SPE J.*, **16**, 1147 (1960).
58. E. Jenckel and F. Nagel, *Kolloid-Z.*, **97**, 37 (1941).
59. H. Onoda and K. Kawata, *Oyo Butsuri*, **27**, 751 (1958); *C.A.*, **53**, 5728e.
60. O. V. Kallistov and E. V. Korneeva, *Vysokomol. Soedin.*, **2**, 1056 (1960).
61. F. Sakaguchi, R. Kitamaru, and W. Tsuji, *Sen-i Gakkaishi*, **23** (1), 18 (1967); *C.A.*, **66**, 105378v.
62. S. M. Savvon and B. A. Margulis, *Vestn. Leningrad. Univ., Fiz. Khim.*, (2), 53 (1970), *C.A.*, **73**, 110282h.
63. A. E. Grishchenko, M. G. Vitovskaya, V. N. Tsvetkov, E. P. Vorob'eva, N. N. Saprykina, and L. I. Mezentseva, *Vysokomol. Soedin., Ser. A.*, **9** (6), 1280 (1967); *Polym. Sci. USSR*, **9**, 1430 (1967).
64. J. F. Rudd and R. D. Andrews, *J. Appl. Phys.*, **31**, 818 (1960).
65. J. F. Rudd, *J. Polym. Sci. B*, **4**, 929 (1966).

66. V. N. Tsvetkov and I. A. Krym, *Vestn. Leningrad. Univ., Fiz. Khim.*, (3), 5 (1956); *C.A.*, **51**, 4043d.
67. J. F. Henderson, K. H. Grundy, and E. Fischer, *J. Polym. Sci. C*, **16** (6), 3121 (1965).
68. E. Fischer and J. F. Henderson, *Rubber Chem. Technol.*, **40**, 1373 (1967).
69. E. Fischer and J. F. Henderson, *J. Polym. Sci. C*, **26**, 149 (1967).
70. V. N. Tsvetkov and M. G. Vitovskaya, *Vysokomol. Soedin.*, **6** (8), 1387 (1964); *Polym. Sci. USSR*, **6**, 1532 (1964).
71. S. I. Sokolov, T. V. Shamrevskaya, and N. A. Shchegolevskaya, *Vysokomol. Soedin.*, **5** (8), 1250 (1963); *Polym. Sci. USSR*, **5**, 322 (1964).
72. T. V. Shamraevskaya, N. A. Shchegolevskaya, and S. I. Sokolov, *Dokl. Akad. Nauk SSSR*, **150** (2), 356 (1963); *C.A.*, **59**, 7715a.
73. T. V. Shamraevskaya and N. A. Shchegolevskaya, *ibid.*, **150** (4), 859 (1963); *C.A.*, **59**, 8887a.
74. E. F. Gurnee, *J. Polym. Sci.*, **41**, 119 (1959).
75. T. J. Hammack and R. D. Andrews, Jr., *J. Appl. Phys.*, **36**, 3574 (1965).
76. Z. Tuji, K. Kawata, and I. Hori, *Brit. J. Appl. Phys.*, **9**, 173 (1958).
77. K. Kawata, *Rikagaku Kenkyusho Hokoku*, **35**, 5 (1959); *C.A.*, **54**, 23407a.
78. V. N. Tsvetkov and A. E. Grishchenko, *J. Polym. Sci. C*, **16** (6), 3195 (1965).
79. M. S. Zlotnikov, I. A. Arbuzova, and E. V. Kuvshinskii, *Mekh. Polim.*, **6** (1), 3 (1970); *C.A.*, **72**, 133471n.
80. F. H. Müller, *Kolloid-Z.*, **95**, 138, 306 (1941).
81. R. S. Stein and A. V. Tobolsky, *Text. Res. J.*, **18**, 201, 302 (1948).

Received September 1, 1971