melting points in the vicinity of 48 °C, the polymer is also similar to POE in its melting behavior.

Acknowledgment. The authors are very grateful to Professor A. Abe for very helpful comments. Thanks are also due to Mr. M. G. Rodriguez who synthesized and fractionated the polymer used in this study. This investigation was supported by a grant of the Comisiõn Asesora de Investigaciõn Científica y Tēcnica.

References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969.
(2) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1111 (1972).
(3) A. Abe and J. E. Mark, *J. Am. Chem. Soc.*, **98**, 6468 (1976).
(4) E. Riande, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2231 (1976).
(5) E. Riande, *Makromol. Chem.*, **178**, 2001 (1977).
(6) K. M. Kelly, G. D. Patterson, and A. E. Tonelli, *Macromolecules*, **10**, 859 (1977).
(7) J. E. Mark, *J. Chem. Phys.*, **67**, 3300 (1977).
(8) E. Riande and J. E. Mark, *Macromolecules*, **11**, 956 (1978).
(9) E. Riande and J. E. Mark, *J. Polym. Sci., Part C*, in press.
(10) Y. Gotoh, H. Sakakihara, and H. Tadokoro, *Polym. J.*, **4**, 68 (1973).
(11) J. E. Mark, *Acc. Chem. Res.*, **7**, 218 (1974).
(12) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Vols. 1 and 2, Elsevier, Amsterdam, 1965.
(13) H. H. Landolt, "Landolt-Börnstein: Zahlenwert und Funktionen aus Physics, Chemistry, Astronomy, Geophysics und Technology", Vol. II, Part 6, Springer, Berlin, 1959.
(14) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); **47**, 573 (1951).
(15) J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950).
(16) K. Nagai and T. Ishikawa, *Polym. J.*, **2**, 416 (1971).
(17) M. Doi, *Polym. J.*, **3**, 252 (1972).
(18) S. C. Liao and J. E. Mark, *J. Chem. Phys.*, **59**, 3825 (1973).
(19) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(20) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 3702 (1966).
(21) A. L. McClellan, "Tables of Experimental Dipole Moments", Vol. I, W. H. Freeman, San Francisco, Calif., 1963; Vol. II, Rahara Enterprises, El Cerrito, Calif., 1974.
(22) A. Abe, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**, 460 (1979).
(23) Y. Takahashi, H. Tadokoro, and Y. Chatani, *J. Macromol. Sci. Phys.*, **2**, 361 (1968).
(24) N. Nogami, H. Sugeta, and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **48**, 3573 (1975); *Chem. Lett.*, 147 (1975).
(25) M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 111 (1977).
(26) A qualitative analysis of the Raman spectra of 2-oxathiahexane (Y. Ogawa, M. Ohta, M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 650 (1977)) seems to suggest that the gauche conformation is as stable as the trans.
(27) Y. Takahashi and J. E. Mark, *Polymer*, **17**, 670 (1976).
(28) D. R. Beech and C. Booth, *J. Polym. Sci., Part B*, **8**, 731 (1970).

Time-Resolved Emission Study of the Poly(*N*-vinylcarbazole)–Dimethyl Terephthalate and Poly(1-vinylnaphthalene)–Dicyanobenzene Interactions

C. E. Hoyle and J. E. Guillet*[1]

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.
Received March 28, 1979

ABSTRACT: Both steady-state and time-resolved emission studies have been made for solutions containing poly(*N*-vinylcarbazole) and dimethyl terephthalate. Fluorescence spectra clearly reveal the presence of both an exciplex and an "exterplex" consisting of two carbazole chromophores and one molecule of dimethyl terephthalate. Similar results were obtained for solutions containing poly(1-vinylnaphthalene) and dicyanobenzene.

Exciplexes formed between an excited aromatic molecule and an electron donor or acceptor molecule have recently received considerable attention.[2] Caldwell et al. found that these highly polar exciplexes can be quenched by an additional electron donor or acceptor molecule to give an excited triplex or "exterplex" made up of three molecules.[3] The exterplex receives its stability from the distribution or separation of charge over three molecules. The exterplex, once it is formed, can reversibly reform the exciplex, or it may return to the ground state of each molecule by nonradiative or radiative decay. In particular, the exterplex formed between two naphthalene molecules and 1,4-dicyanobenzene (DCNB) has been studied throughly by Mimura and Itoh.[4] They found that in a concentrated solution of 2-methylnaphthalene, addition of DCNB quenched the naphthalene monomer and excimer emission with the appearance of both an exciplex emission (λ_{max} ~420 nm) and an exterplex emission (λ_{max} ~490 nm). The two peaks responsible for the exciplex and exterplex emission were fully resolved by decay and time resolved fluorescence measurements. In additon, they found that the exterplex formed between the two naphthalene chromophores of 1,3-dinaphthylpropane and DCNB was identical with the exterplex formed between two separated naphthalene molecules and DCNB. In order to extend these results to polymers and understand the exterplex formation between excited pendant aromatic chromophores on various polymers and small molecule ground state electron donor or acceptor molecules, it is first necessary to consider briefly the photophysical properties of polymers with repeating aromatic chromophores.

The emission spectra of several polymers in dilute solution, such as poly(1-vinylnaphthalene) (PVN) and poly(*N*-vinylcarbazole) (PVCz), are characterized by emission from excimers formed from two neighboring pendant aromatic groups on the same polymer chain.[5] The low-energy sandwich-type excimers of PVN (λ_{max} ~400 nm) and PVCz (λ_{max} ~420 nm) are accompanied by emission from a monomer state (λ_{max} ~355)[6] and a higher-energy excimer state (λ_{max} ~370 nm),[7] respectively.

The fluorescence emissions of both PVN and PVCz are readily quenched in the presence of small-molecule electron acceptors. For instance, the fluorescence of PVCz is greatly diminished when dimethyl terephthalate (DMTP) is added to either a solution or film of PVCz.[8] The quenching process is accompanied by the appearance

0024-9297/79/2212-0956$01.00/0 © 1979 American Chemical Society

of a broad, red-shifted, structureless emission. This new emission has been attributed to the fluorescence from an exciplex (formed between a pendant carbazole chromophore (Cz) and a DMTP molecule (Cz^+–$DMTP^-$)*) and an exterplex formed between two carbazole chromophores and DMTP[9]

$$\overset{+}{\overline{Cz\text{–}Cz}}\text{–}DMTP^-$$

In contrast, emission from *N*-ethylcarbazole (EtCz) quenched by DMTP occurs from a single exciplex state ($EtCz^+$–$DMTP^-$)*. The present paper characterizes and identifies the exterplexes formed in the PVCz–DMTP and PVN–DCNB systems in solution, using a single-photon counting apparatus adapted for time-resolved emission spectra.

Experimental Section

Poly(*N*-vinylcarbazole) (Monomer-Polymer) was precipitated several times into methanol and was found to have a viscosity average molecular weight of 1.2×10^6. Poly(1-vinylnaphthalene) was prepared by spontaneous polymerization and purified by successive precipitation from benzene solution into methanol, after which the molecular weight was between 5000 and 10 000. *N*-Ethylcarbazole (Eastman) was recrystallized several times from an ethanol–benzene solution. Dimethyl terephthalate was recrystallized several times in benzene and then vacuum sublimed. The DCNB was recrystallized several times from benzene. No traces of anthracene could be detected in any of the samples. Spectroanalyzed benzene (Fisher) was refluxed twice over P_2O_5 for 24 h and distilled each time, keeping only the middle third.

Steady-state fluorescence spectra (uncorrected for phototube response) were measured on a Hitachi MPF-2A spectrometer (the one corrected maximum was determined by using a quinine sulfate standard in 1 N H_2SO_4.) The single-photon counting apparatus was modified for time-resolved spectroscopy and has been described previously.[10] The time settings are given as the time difference of the upper (or lower) limit (determined by the discriminator settings on the analogue-to-digital converter) from the maximum of the exciting lamp.[11] The time-resolved spectra are not corrected for phototube response.

Results and Discussion

The steady-state fluorescence spectra of PVCz and EtCz in the presence of DMTP have been discussed in a previous communication.[9] The fluorescence from the ($EtCz^+$–$DMTP^-$)* exciplex has a maximum at ca. 460 ± 10 nm. The PVCz–DMTP emission is characterized by a very broad, structureless emission with a maximum at 495 ± 10 nm (520 ± 10 nm if corrected for phototube response). From the double-exponential decay curve of the PVCz–DMTP emission when viewed above 520 nm (using a 3-69 Corning filter), it was concluded that at least two emitting species are responsible for the fluorescence in this region. This may be due to emission from both an exciplex (λ_{max} ~460 nm) and an exterplex (λ_{max} ~495 nm). The PVCz excimer emission is greatly reduced, has a low fluorescence intensity, and probably does not contribute significantly to the decay curve when viewed at wavelengths above 520 nm. In order to further resolve the PVCz–DMTP emission spectrum, it is helpful to take time-resolved emission spectra at various time intervals (Figure 1). The spectrum in curve a, taken at the shortest time interval, shows emission from only the second excimer emission of PVCz at λ_{max} ~370 nm. No emission from the low-energy sandwich excimer (λ_{max} ~420 nm), the exciplex (λ_{max} ~460 nm), or the exterplex (λ_{max} ~495 nm) can be seen on this time scale. At a slightly longer time interval (curve b), fluorescence from the low-energy excimer at 420 nm and a broad peak above 450 nm is also present. At even longer time intervals (curve c), the emission above 450 nm becomes increasingly larger with respect to

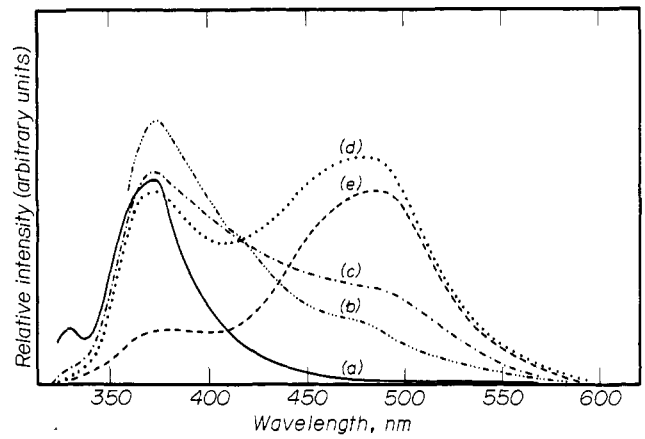


Figure 1. Time-resolved fluorescence spectra of PVCz (5×10^{-4} M)–DMTP (0.07 M) in degassed benzene at 23° C; excitation wavelength, 330 nm; slit widths, 1.25 mm. Time settings: (a) upper limit 0.23 ns from lamp maximum; (b) lower limit 3.68 ns and upper limit 8.51 ns from lamp maximum; (c) lower limit 7.82 ns and upper limit 13.11 ns from lamp maximum; (d) lower limit 13.11 ns and upper limit 17.71 ns from lamp maximum; (e) lower limit 17.71 ns and upper limit 25.07 ns from lamp maximum. Spectra are not corrected for phototube response and are not on the same absolute scale.

Table I
Uncorrected Peak Emission Maxima for PVCz-DMTP and EtCz-DMTP Systems

	wavelength max, nm	
	single-photon counting[a]	steady state
high-energy excimer	372	372[b]
low-energy excimer	417	420[b]
exciplex	455	460[c]
exterplex	495	495[d] (520[e])

[a] Determined from a PVCz (5×10^{-4} M)–DMTP (0.07 M) degassed benzene solution. Directly from multichannel analyzer storage of the time-resolved single-photon counting apparatus. Not corrected for phototube response. [b] Determined from a steady-state emission spectrum of a PVCz (5×10^{-4} M) degassed benzene solution. Not corrected for phototube response. [c] Determined from a steady-state emission spectrum of EtCz (5×10^{-4} M)-DMTP (0.07 M) degassed benzene solution. Not corrected for phototube response. [d] Determined from a steady-state emission spectrum of PVCz (5×10^{-4} M)-DMTP (0.07 M) degassed benzene solution. Not corrected for phototube response. [e] Determined from a steady-state emission spectrum of a PVCz (5×10^{-4} M)-DMTP (0.07 M) degassed benzene solution. Corrected for phototube response.

emission from the high-energy excimer (λ_{max} ~370 nm). At very long time intervals (curves d and e), the emission intensity above 450 nm becomes dominant with respect to the second PVCz excimer, which on the longest time scale (curve e) is very small. The emission above 450 nm is assigned to the emission from a combination of the (Cz^+–$DMTP^-$)* exciplex and the

$$\overset{+}{\overline{Cz\text{–}Cz}}\text{–}DMTP^-$$

exterplex, where Cz is a carbazole chromophore pendant to a polymer chain. The uncorrected maxima for the high-energy excimer, the low-energy excimer, and the exterplex for the PVCz–DMTP system were determined directly from the intensity data (counts per channel) stored in the multichannel analyzer of the single-photon counting apparatus and are shown in Table I. The steady-state maxima obtained for the high-energy excimers of PVCz (5×10^{-4} M solution) as well as the emission maxima for

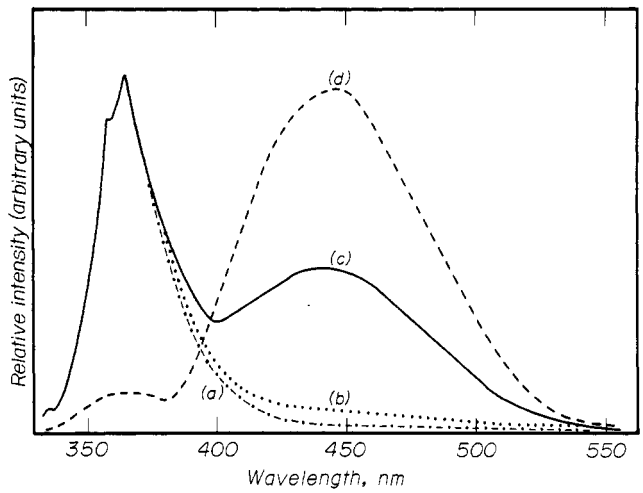


Figure 2. Time-resolved fluorescence spectra of EtCz (5×10^{-4} M)–DMTP (0.07 M) in degassed benzene at 23 °C; excitation wavelength, 330 nm; slit widths, 1.25 mm. Time settings: (a) upper limit 0.00 ns from lamp maximum; (b) lower limit 0.00 ns and upper limit 3.22 ns from lamp maximum; (c) lower limit 3.91 ns and upper limit 11.04 ns from lamp maximum; (d) lower limit 11.27 ns and upper limit 24.84 ns from lamp maximum. Spectra are not corrected for phototube response and are not on the same absolute scale.

the EtCz–DMTP exciplex are also given in Table I. The agreement between these maxima is remarkable and provides additional evidence for the existence of both the exciplex and the exterplex.

Further understanding of the PVCz–DMTP system can be obtained by consideration of the time-resolved fluorescence of the model EtCz–DMTP system (Figure 2). The spectrum on the shortest time scale (curve a) shows emission from only the EtCz monomer. The emission from the exciplex is totally absent on this short time scale. On longer time scales (curves b, c, and d), the exciplex emission (λ_{max} ~460 nm) continually increases with respect to the monomer emission. At the longest time interval (curve d), the exciplex emission completely dominates the monomer emission. From these results, it is obvious that only the EtCz monomer emission and the $(EtCz^+–DMTP^-)^*$ exciplex emission are responsible for the emission of the EtCz–DMTP system. This concurs with the results of emission lifetimes measured previously.[9] From the results of the EtCz–DMTP and the PVCz–DMTP systems, it is difficult to assign the exact sequence of the formation of the low-energy excimer (λ_{max} ~420 nm), the exciplex (λ_{max} ~460 nm), and the exterplex (λ_{max} ~495 nm) in the PVCz–DMTP system. It is obvious that all are formed subsequent to the high-energy excimer, which appears to be formed immediately (<1 ns) after the lamp flash.[10] The question of the sequence of formation of the excited states will be considered in greater detail after the results from the PVN–DCNB system have been considered.

The lifetimes of the low-energy excimer and the exciplex are 39 ± 3 and 71 ± 2 ns, respectively. The lifetime of the high-energy excimer is complex and difficult to determine (see ref 7 for a discussion of this problem), but it is not more than 15 ns. The lifetime of the exterplex is equally difficult to measure, but it is most likely longer lived. From consideration of the lifetime (decay) data, it can be concluded that the exterplex and exciplex will be prominent at longer times where the high-energy excimer emission is decreased (due to its shorter lifetime (≤15 ns)). This is consistent with Figure 1e.

Poly(vinylnaphthalene) shows many similar features to PVCz in solution. The time-resolved emission spectra of

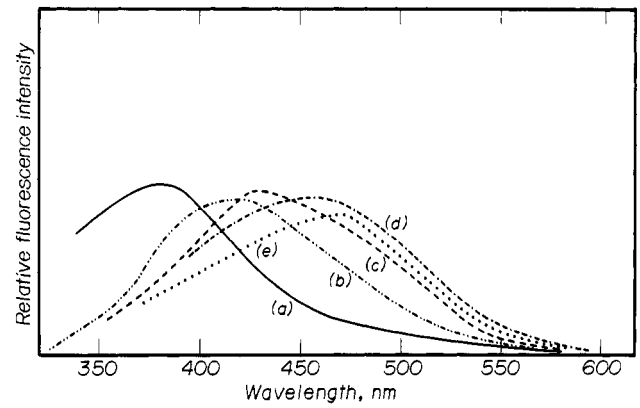
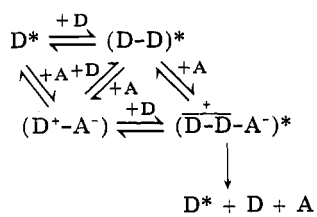


Figure 3. Time-resolved fluorescence spectra of PVN (4×10^{-4} M)–DCNB (8×10^{-2} M) in degassed benzene at 23 °C; excitation wavelength, 320 nm; slit widths, 1.25 mm. Time settings: (a) upper limit 5.9 ns from lamp maximum; (b) lower limit 5.9 ns and upper limit 26.5 ns from lamp maximum; (c) lower limit 26.5 ns and upper limit 100.0 ns from lamp maximum; (d) lower limit 105.8 ns and upper limit 223.4 ns from lamp maximum; (e) lower limit 223.4 ns and upper limit 338.1 ns from lamp maximum. Spectra are not corrected for phototube response and are not on the same absolute scale.

Scheme I



a PVN (4×10^{-4} M) and DCNB (8×10^{-2} M) solution in benzene are given at several times in Figure 3. At times less than 6 ns from the lamp maximum (curve a), emission arises almost exclusively from the excimer at λ_{max} ~390 nm. At later times (5.9 to 26.5 ns, curve b), the exciplex emission, with a maximum at about 420 nm, as well as the excimer emission, is present. No significant emission from any other state could be identified from the spectrum in curve b. At later times (curve c, Figure 3), the emission spectrum is broadened and shifted to even longer wavelengths. In curves d and e, it is apparent that a new peak with a maximum around 480 nm appears, with a concomitant decrease in the relative emission from the exciplex (λ_{max} ~420 nm). The spectra shown in Figure 3 are very similar to the time-resolved spectra of both the 1,3-dinaphthylpropane–DCNB system and concentrated 2-methylnaphthalene solutions in the presence of DCNB.[4] Furthermore, it was concluded that in the case of the 1,3-dinaphthylpropane–DCNB system, the exciplex forms before the exterplex. From curve b, Figure 3, little or no exterplex emission is present, but the exciplex has already formed at this time. Only at later times does the exterplex form. Thus, the exterplex formed in the PVN–DCNB system, as in the case of 1,3-dinaphthylpropane–DCNB, is preceded by exciplex formation.

Scheme I presented below shows the possibilities of interconversion between a donor monomer D, the excimer (D–D)* formed between two donors, the exciplex (D–A)* formed between an excited donor and a ground state acceptor A, and the exterplex

$$(\overset{+}{\text{D}}\text{–}\overset{}{\text{D}}\text{–A}^-)^*$$

formed between two donors and an acceptor. Paths for nonradiative and radiative decay from the four states

under consideration are not included. In the case of PVN, 1,3-dinaphthylpropane, or 2-methylnaphthalene with the DCNB acceptor, it has been concluded that the exterplex is formed from attack of a naphthalene donor D on the naphthalene–DCNB(D^+–A^-)* exciplex. Such a mechanism seems quite reasonable since attack of the highly polar exciplex ($\mu_e > 10$ D) by an electron donor would stabilize the complex by distributing the positive charge over two naphthalene chromophores. An attack of the nonpolar excimer could result in the exciplex or the exterplex. If the exciplex were formed, it would be highly susceptible to attack by the neighboring naphthalene partner of the original naphthalene–naphthalene excimer. It is difficult to suggest this same mechanism for the PVCz–DMTP system from the time-resolved spectra given in Figure 1. It may be that the pathway proceeding through the polar exciplex is the major pathway for exterplex formation. However, direct formation of the exterplex by attack of the carbazole sandwich excimer by DMTP cannot be excluded. In both cases, the stability of the exterplex is provided by the distribution of the positive charge over the two donor chromophores.

It appears that the polymer chain provides an excellent structure for holding a second aromatic chromophore in the position required for the exterplex formation since these do not form in simple small-molecule models. Furthermore, the unique separation of charge which occurs in the PVN–DCNB or PVCz–DMTP systems may be simple analogues for the process of charge separation in photosynthesis.[12] Also, it may be possible to quench the exterplex emission effectively. This would provide a mechanism for transfer of electron density from an electron donor to the electron acceptor (DMTP) separated by the two carbazole chromophores and the polymer. Such electron-transfer reactions could be of some importance in natural or synthetic photochemical energy conversion schemes.

Acknowledgment. The authors wish to acknowledge the generous financial support of this work by the National Research Council of Canada.

References and Notes

(1) Address correspondence to this author.
(2) F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, **97**, 5950 (1975); **98**, 4338 (1976); **99**, 3779 (1977); D. Rehm and A. Weller, *Isr. J. Chem.*, 8, 259 (1970); N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975); D. A. Labianca, G. N. Taylor, and G. S. Hammond, *ibid.*, **94**, 3679 (1972); M. Gordon and W. R. Ware, Ed., "The Exciplex", Academic Press, New York, 1975.
(3) R. A. Caldwell, D. Creed, and H. Ohta, *J. Am. Chem. Soc.*, **96**, 2994 (1974); D. Creed and R. A. Caldwell, *ibid.*, **96**, 7369 (1974); H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *ibid.*, **98**, 2002 (1976).
(4) T. Mimura and M. Itoh, *J. Am. Chem. Soc.*, **98**, 1095 (1976).
(5) W. Klöpffer, "Intermolecular Excimers in Organic Molecular Photochemistry", J. B. Birks, Ed., Wiley-Interscience, New York, 1973, p 357.
(6) M. T. Vala, J. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).
(7) G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
(8) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2082 (1976); G. Pfister, D. J. Williams, and G. E. Johnson, *J. Phys. Chem.*, **78**, 2009 (1974); K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 2613 (1973).
(9) C. E. Hoyle, T. L. Nemzek, A. Mar, and J. E. Guillet, *Macromolecules*, **11**, 429 (1978).
(10) C. E. Hoyle and J. E. Guillet, *Macromolecules*, **11**, 221 (1978).
(11) S. Georghiou, *Nature (London)*, **259**, 423 (1976).
(12) R. A. White and G. Tollin, *Photochem. Photobiol.*, **14**, 43 (1971); J. R. Harbour and G. Tollin, *ibid.*, **20**, 271 (1974).

Melt Rheology of Four-Arm and Six-Arm Star Polystyrenes

W. W. Graessley and J. Roovers*

Department of Chemical Engineering and the Department of Materials Science, Northwestern University, Evanston, Illinois 60201, and the National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R9.‡ *Received March 28, 1979*

ABSTRACT: The dynamic moduli of linear, four-arm and six-arm star polystyrene melts were measured over a wide range of frequencies and temperatures by the eccentric rotating disk method. The zero-shear viscosities of the star polystyrenes were less than those linear polystyrenes of the same molecular weight ($M < 10^6$). However, viscosities of the high molecular weight stars were larger when comparisons were made at a constant radius of gyration. The observed enhancements agree with those found in polybutadiene stars when compared on the basis of the parameter $Z(M_{br}/M_e)$, where Z and M_e are constants characteristic of each polymer, and M_{br} is the molecular weight of the arm. The zero-shear recoverable compliance of the star polymers is well-described by the Rouse–Ham formula $J_e^0 = 0.4g_2\rho RT/M$. The plateau modulus G_N^0 appears to be the same for linear and star polystyrenes. The frequency dependence of the dynamic moduli was examined for the possible presence of a second relaxation mechanism in high molecular weight stars, giving rise to viscosity enhancement, which is absent in the terminal spectrum of linear polymers.

The steady flow properties of polymer melts are usually characterized by viscosity and recoverable shear compliance. At sufficiently low shear rates (the zero-shear limit), both material properties become constants, η_0 and J_e^0. Studies of zero-shear viscosity in numerous linear random-coil polymers of narrow molecular weight distribution have now clearly established two regions. For low molecular weight polymers, η_0 is directly proportional to molecular weight M; for high molecular weight polymers, η_0 is proportional to $M^{3.4}$. A molecular weight characteristic of the polymer, M_c, separates the two regions.[1-3] Two regions have also been established for the zero-shear recoverable compliance. At low molecular weights, J_e^0 is directly proportional to M; at high molecular weights, J_e^0 is independent of molecular weight. A second characteristic molecular weight, M_c', separates the two regions.[3]

* Address correspondence to this author at the National Research Council of Canada.
‡ Issued as NRCC No. 17649.

0024-9297/79/2212-0959$01.00/0 © 1979 American Chemical Society