combinations of incident and scattered polarizations with those predicted by group theoretical analysis of an isolated chain in either a 3/2-helical or planar-zigzag conformation.

Observation of the Raman-active LAM and the correlation of its position with the corresponding stem length in lamellar crystals provide further evidence of a trans-planar structure.

Combined infrared and Raman measurements in the CH stretching region indicate, based on local symmetry arguments, that the CC bond joining the two CH_2 groups must be trans. Although this constitutes a necessary but not sufficient condition for planarity, when taken collectively with the additional results already described, it strongly supports the existence of a planar structure for the E–TFE copolymer in the solid state, as has been predicted by Farmer and Lando.[14]

Acknowledgment. We thank E. S. Clark (University of Tennessee) and T. Russell (IBM) for obtaining the WAXS and SAXS photographs of the E–TFE copolymer filament.

Registry No. E–TFE, 25038-71-5.

References and Notes

(1) Carter, V. B. *J. Mol. Spectrosc.* **1970**, *34*, 356.
(2) Bailey, R. T.; Hyde, A. J.; Kim, J. J. *Spectrochim. Acta, Part A* **1974**, *30A*, 91.
(3) Boerio, F. J.; Bailey, R. A. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 433.
(4) Bailey, R. T.; Hyde, A. J.; Kim, J. J.; McLeish, J. *Spectrochim. Acta, Part A* **1977**, *33A*, 1053.
(5) Rabolt, J. F.; Fanconi, B. *Macromolecules* **1978**, *11*, 740.
(6) Satija, S.; Wang, C. H. *J. Chem. Phys.* **1978**, *69*, 2739.
(7) Abenoza, M.; Armengaud, A. *Polymer* **1981**, *22*, 1341.
(8) Modena, M.; Garbuglio, C.; Ragazzini, M. *J. Polym. Sci., Polym. Lett. Ed.* **1972**, *10*, 153.
(9) Pireaux, J. J.; Riga, J.; Caudano, R.; Verbist, J.; Gobillon, Y.; Delhalle, J.; Delhalle, S.; Andre, J. M. *J. Polym. Sci., Part A-1* **1979**, *17*, 1175.
(10) English, A. D.; Garza, O. T. *Macromolecules* **1979**, *12*, 351.
(11) Clark, D. T.; Feast, W. J.; Ritchie, I.; Musgrave, W. K. R.; Modena, M.; Ragazzini, M. *J. Polym. Sci., Part A-1* **1974**, *12*, 1049.
(12) Garbuglio, C.; Modena, M.; Valera, M.; Ragazzini, M. *Eur. Polym. J.* **1974**, *10*, 91.
(13) Wilson, F. C.; Starkweather, H. W., Jr. *J. Polym. Sci., Part A-2* **1973**, *11*, 919.
(14) Farmer, B. L.; Lando, J. B. *J. Macromol. Sci., Phys.* **1975**, *B11*, 89.
(15) Devlin, G. E.; Davis, J. L.; Chase, L.; Geschwind, S. *Appl. Phys. Lett.* **1971**, *19*, 138.
(16) Snyder, R. G.; Scherer, J. R. *J. Polym. Sci., Part A-2* **1980**, *18*, 421.
(17) Billmeyer, F. W., Jr. In "Textbook of Polymer Science"; Wiley: New York, 1971.
(18) Kobayashi, M.; Tashiro, K.; Tadokoro, H. *Macromolecules* **1975**, *8*, 158.
(19) Alexander, L. E. In "X-Ray Diffraction Methods in Polymer Science"; Wiley-Interscience: New York, 1969.
(20) Damen, T. C.; Porto, S. P. S.; Tell, B. *Phys. Rev.* **1966**, *142*, 570.
(21) Snyder, R. G. *J. Mol. Spectrosc.* **1971**, *37*, 353.
(22) Schlotter, N. E.; Rabolt, J. F., to be published.
(23) Hsu, S. L.; Sibilia, J. P.; Obrien, K. P.; Snyder, R. G. *Macromolecules* **1978**, *11*, 990.
(24) Hendra, P. J.; Jobic, H. P.; Marsden, E. P.; Bloor, D. *Spectrochim. Acta, Part A* **1977**, *33A*, 445.
(25) Campos-Vallette, M.; Rey-Lafon, M. *J. Chem. Phys.*, in press.
(26) Strobl, G. R.; Hagedorn, W. *J. Polym. Sci., Part A-2* **1978**, *16*, 1181.
(27) Fanconi, B.; Crissman, J. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 421.
(28) Shimanouchi, T.; Tasumi, M. *Indian J. Pure Appl. Phys.* **1971**, *9*, 958.
(29) Reneker, D. H.; Fanconi, B. *J. Appl. Phys.* **1975**, *48*, 4144.
(30) Schaufele, R. F.; Shimanouchi, T. *J. Chem. Phys.* **1967**, *47*, 3605.
(31) Rabolt, J. F.; Fanconi, B. *Polymer* **1977**, *18*, 1258.

Effect of Polymer Chain Tacticity on the Fluorescence of Molecular Rotors

Rafik O. Loutfy*

Xerox Research Centre of Canada, 2480 Dunwin Drive,
Mississauga, Ontario L5L 1J9, Canada

David M. Teegarden†

Webster Research Center, Xerox Corporation, Webster, New York 14580.
Received January 14, 1982

ABSTRACT: The fluorescence properties of julolidinemalononitrile (1), a molecular rotor probe, have been studied in a series of stereoregular poly(methyl methacrylate) films. The quantum yield of fluorescence of 1 was found to be dependent on the tacticity of the polymer. The relatively high fluorescence yield of 1 in isotactic PMMA indicated that the flexibility of isotactic chains is lower than that of syndiotactic or atactic PMMA. The temperature-dependent fluorescence results are consistent with a helical conformation for isotactic PMMA.

In recent years methods have become known for the preparation of high molecular weight stereoregular isotactic and syndiotactic poly(methyl methacrylate),[1] (*i*- and *s*-PMMA) (see Figure 1). These species exhibit vastly different properties from the so-called atactic (a-PMMA) or random polymers. Both the isotactic and syndiotactic PMMA polymers have been characterized through differences in X-ray diffraction patterns,[2] infrared spectra,[3] laser Raman spectra,[3] far-ultraviolet spectra,[4] densities,[5] glass transition temperature,[6] dielectric loss curves,[7] and mechanical and viscoelastic properties.[8] Information on the steric arrangements of functional groups is best provided by high-resolution NMR techniques.[9]

Although certain of these measurements have given direct information on the tacticity of these polymers, the

---

†Present address: Department of Chemistry, St. John Fisher College, Rochester, NY 14618.

0024-9297/83/2216-0452$01.50/0

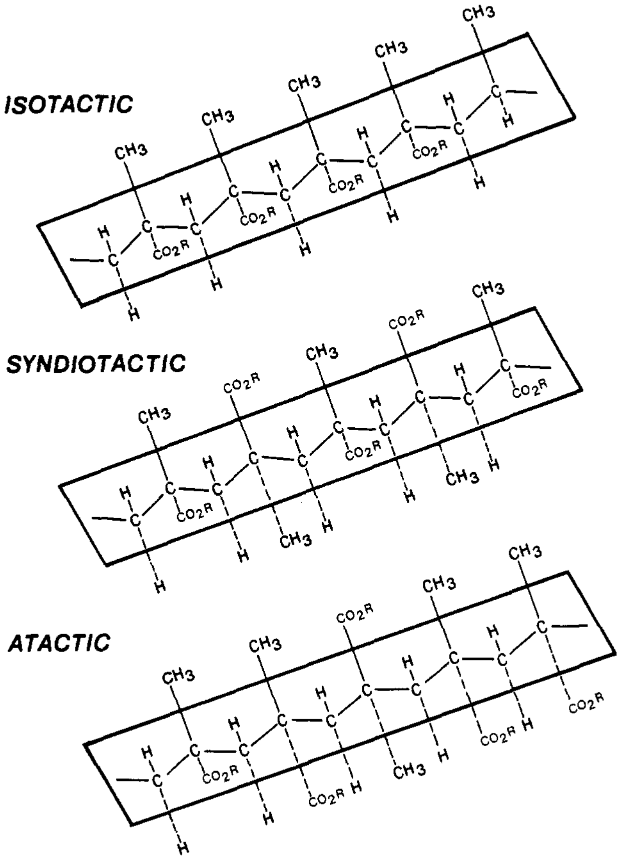


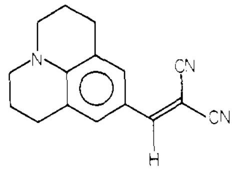
Figure 1. Chemical structure of stereoregular poly(methyl methacrylate).

conformational structure of these macromolecules is still a matter of debate.[4,10-13]

Liquori and co-workers[4] proposed a fivefold helical conformation for isotactic PMMA, with a repeat distance of 10.4 Å. However, Tadokoro and co-workers,[12] using X-ray data, derived a double-helical structure, in which each strand consists of ten repeat units per turn, with repeat distance of 20.8 Å. Recently, Sundararajan,[13] using virtual bond analysis, showed that the isolated 10-unit helix is, indeed, of lower energy than the 5-unit helix by about 2.8 kcal/mol. Furthermore, the transition of 43 °C exhibited by isotactic PMMA was suggested to be due to chain transformation from (5/1) to (5/2) helix by Liquori[10,11] and to transition between the (5/2) to (10/2) helices by Sundararajan.[13] Evidently, an alternative method for determining the conformational structure of stereoregular polymers is still needed. Such a technique should probe the microstructure of the polymer and account satisfactorily for the dynamic structural changes occurring over a wide temperature range. At the same time, the measurement should not induce modification in the chemistry or structure of the polymer and it should be simple.

In recent years the application of luminescence spectroscopy for the study of great diversity of phenomena occurring in synthetic and natural polymers has become widespread.[14-18] The versatility and sensitivity of luminescence as a technique in polymer chemistry stem from the multiple aspects of the interaction of electronically excited states with their immediate environment. We have recently described a novel phenomenon associated with the effect of media rigidity on the fluorescence intensities of a series of donor–acceptor dyes, [*p*-(dialkylamino)-benzylidene]malononitriles.[19] The singlet-excited-state lifetime of these dyes is estimated to be 3–10 ps in solution, which corresponds to a nonradiative decay rate, k_{nr}, of the order of 10^{11} s^{-1}. The extremely fast deactivation rate of the singlet state of these materials was attributed to torsional relaxation. We have shown that environmental factors restricting the internal molecular rotation of these dyes lead to a decrease in k_{nr} and consequently an increase in fluorescence yield. These dyes are, therefore, excellent microscopic probes for measuring the torsional rigidity of the surrounding polymer media, and their fluorescence yield is very sensitive to dynamic structural changes occurring over wide temperature range.

Here the results of an investigation concerning the emission properties of julolidinemalononitrile (1) in solid films of stereoregular poly(methyl methacrylate) are reported. The quantum yield of fluorescence of 1 is found to be dependent on the tacticity of PMMA. We also examined the dependence of the fluorescence intensity of 1 in solid PMMA films on temperature. The transition at ~43 °C for i-PMMA was clearly observed and is consistent with unwinding of a helix.



1

Experimental Section

Materials. Julolidinemalononitrile (1) was purified as described previously.[20] Atactic poly(methyl methacrylate) samples were obtained from Polysciences Inc. as standards with narrow molecular weight distribution. Isotactic poly(methyl methacrylates) were obtained by polymerization of methyl methacrylate using phenylmagnesium bromide or lithium aluminum hydride initiators.[21-23] Syndiotactic poly(methyl methacrylate) was prepared as described elsewhere[24] using ethyl(pentamethyleneimino)magnesium initiator. All polymerizations were carried out in an inert atmosphere with syringe technique. The reactions were quenched by precipitation in a large excess of methanol containing a small amount of HCl and the solids filtered, washed, and dried. The crude products were then stirred in 10% aqueous HCl solution, washed thoroughly with water, dried, dissolved in benzene, and freeze-dried.

Molecular Weight Determination. The intrinsic viscosity, $[\eta]$, of all polymers studied was determined in chloroform at 30 °C with a dilution viscometer. Molecular weight distributions and M_w's were determined by gel permeation chromatography, the latter being calculated as a Q factor.

Tacticity Determination. Tacticities are expressed as triads on the basis of proton NMR spectra obtained on a Bruker WP-80 Fourier transform spectrometer. Spectra were obtained in nitrobenzene-d_5 solution at 100–110 °C with Me_4Si as internal standard. These analyses, along with the molecular weight data, are summarized in Table I, where i, h, and s are the fractional isotactic, heterotactic, and syndiotactic triad contents, respectively.

Determination of the Glass Transition Temperature. The glass transition temperature T_g of each polymer studied was determined by differential scanning calorimetry using a Du Pont DSC apparatus. A typical DSC thermogram is shown in Figure 2. The thermal history of the sample greatly influenced the appearance of the first DSC curve. In general, several DSC runs were made with each polymer and the average of all runs was used to determine T_g. T_g was obtained from the intersection of the initial base line and the sloping portion of the curve and is accurate to about ±2 °C. The results are given in Table II. The glass transition temperature of PMMA is strongly tacticity dependent. Our result is in fairly good agreement with literature data.[25]

Dye-in-Polymer Film Preparation. Films of the dye 1 (0.05 wt %) in poly(methyl methacrylate) were prepared by solvent casting from a 10% solution of solid polymer dissolved in methylene chloride. Typically 100 mg of PMMA was dissolved in 1 mL of 2×10^{-4} M 1 in methylene chloride. Films were cast

Table I
Preparation of Stereoregular Poly(methyl methacrylate)

$$\text{MMA} \xrightarrow{\text{initiator}} \text{PMMA}$$

				tacticity, triads %		
stereoregularity	initiator	$M_w \times 10^{-3}$	MWD	*i*	*h*	*s*
isotactic	PhMgBr	61	3.2	>98		
	$LiAlH_4$	80	1.8	96	3	1
	PhMgBr	82	3.2	>98		
atactic	free radical	75	1.04	6	36	58
		81.8	1.75			
		250	1.04		(approx the same)	
syndiotactic	$EtMgN(CH_2)_5$	90	2.3	<1	23	77
	$EtMgN(CH_2)_5$	180	1.3	<1	23	77

Table II
Spectroscopic Data for Julolidinemalononitrile in Various Stereoregular PMMA

				absorption and fluorescence data		
	$M_w \times 10^{-3}$	MWD	T_g, °C	λ_{max}, nm	λ_F, nm	Φ_f
isotactic	82	3.2	52	457.5	492	0.049
	61	3.2	46	458	492	0.043
	80	1.8	44	458	493	0.036
atactic	75	1.04	100	450	491	0.022
	81.8	1.75	104	450	491	0.020
	250	1.04	110	450	492	0.018
syndiotactic	90	2.3	123	452	490	0.020
	180	1.3	122	453	490	0.015

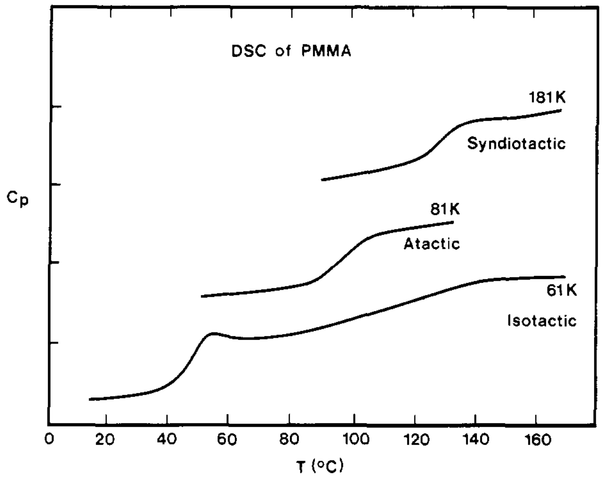


Figure 2. Differential scanning thermogram of i-, a-, and s-PMMA.

by placing part of the prepared solution onto precleaned 2 × 2 in. Corning glass plates. The glass plates were covered and the solvent was allowed to slowly evaporate at room temperature. The resulting films were typically about 8 μm thick. The films were then placed in a small vacuum oven for 24 h. The emission spectrum of a film measured immediately following the room-temperature evaporation was not different from the emission spectrum measured following days of storage under vacuum.

Fluorescence Measurements. The measurements were done at relatively low dye concentration to avoid dye aggregation and dimer formation. Fluorescence spectra of the films were recorded by front-surface illumination on a Perkin-Elmer MPF4 spectrofluorimeter, which was equipped with a differential corrected spectral unit (DCSU-2). Fluorescence quantum yields were determined (in a corrected mode) by comparing with 9,10-diphenylanthracene fluorescence in PMMA (3×10^{-3} M), which has been shown to have a quantum yield of 0.99.[26] The optical densities of the dye in polymer samples were in the range of 0.3–0.5 at the absorption maximum. Controlled experiments showed that the polymer film itself did not show any absorption or emission under the experimental conditions. The temperature-dependent fluorescence measurements were carried out by using a specially designed electrically heated copper block that was fitted into the sample compartment. Thermal grease was employed to contact the Corning glass plate to the copper block. The temperature of the copper block was controlled by the amount of current supplied to the heater. The polymer film temperature was monitored at the surface with a skin surface thermocouple probe (Bailey SST-1) connected to Bailey Instrument digital meter (Model BAT-12).

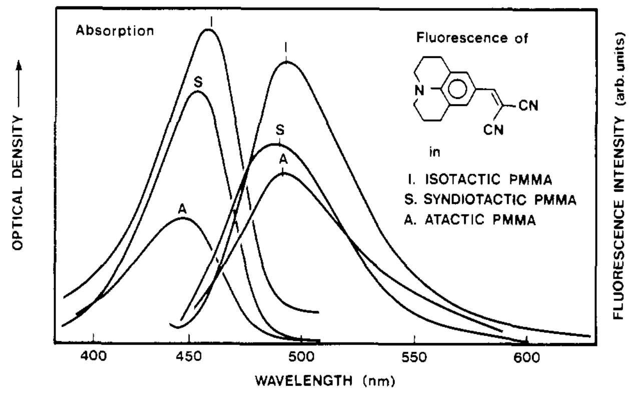


Figure 3. Absorption and fluorescence emission bands of julolidinemalononitrile in PMMA's film.

The absorption spectra of the dye 1 in PMMA films were measured on a Cary 17 spectrometer. Summaries of the absorption and fluorescence data are given in Table II. The absorption and emission maxima of 1 have been previously found to shift to the red as the dielectric constant of the solvent (medium) increases.[19] Figure 3 shows a small red shift in the absorption maximum of 1 in i-PMMA relative to that in s- or a-PMMA. These results suggest that the dielectric constant of i-PMMA is slightly higher than that of s- or a-PMMA.

Results and Discussion

Figure 3 displays the absorption and emission spectra of julolidinemalononitrile (1) in films of stereoregular poly(methyl methacrylate). The dye 1 exhibits an intense absorption at λ_{max} ~450 nm and weak fluorescence emission band at λ_{max} 490 nm. The similarity of the absorption and emission bands of 1 in PMMA to that in ethyl acetate indicates that there is no specific interaction between the dye and the polymers. The $S_0 \rightarrow S_1$ transition of 1 was previously assigned to an intramolecular charge-

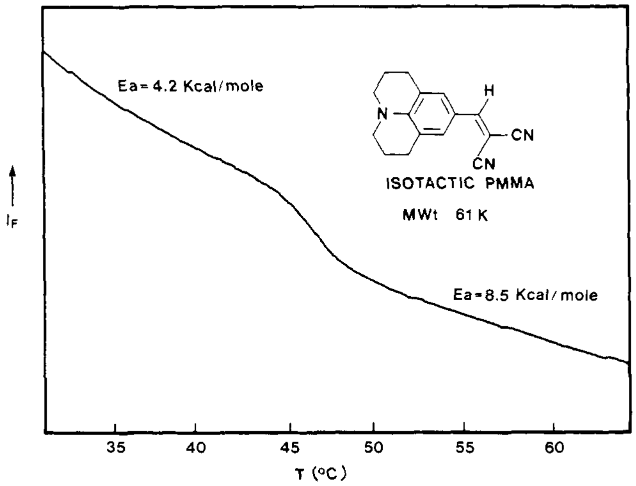


Figure 4. Temperature-dependent fluorescence of 1 in isotactic PMMA (M_w = 61 000).

transfer state (D^+–A^-).[19] The radiative rate constant, k_r, of the emitting single excited state of 1 is 2.8×10^8 s^{-1} (i.e., τ_r = 3.6 ns), while the nonradiative decay rate, k_{nr}, is of the order of 10^{11} s^{-1}. The extremely fast deactivation rate of the singlet excited state of 1 and many intramolecular change-transfer complexes is attributed to fast intrinsic *internal rotation,* a process involving movement of one part of the molecule with respect to the other. Environmental factors restricting the internal rotation of the dye lead to decreases in k_{nr} and consequently increases in fluorescence.

For dyes with rotation-dependent nonradiative decay, k_{nr}, the fluorescence quantum yield becomes very sensitive to media rigidity, viscosity, polarity, and temperature.[19,27] The data in Table II show that dye 1 fluorescence is also sensitive to the tacticity of the polymer matrix. The quantum yield for fluorescence of 1 is markedly enhanced in isotactic poly(methyl methacrylate) as compared to the syndiotactic or atactic polymers. The enhancement of fluorescence of 1 is caused by inhibition of the internal molecular rotation via rigidization of the probe by local environment. These results indicate that the flexibility of isotactic chains is lower than that of syndiotactic or atactic chains. Vitagliano and co-workers[28] have recently found that the probability of cationic dye (Acridine orange) intercalation in isotactic polyacids is much higher than that in syndiotactic ones. It is, therefore, tempting to speculate that the relatively high fluorescence yield of 1 in isotactic PMMA is due to rigidization of the probe by a helical conformation of the polymer chains. The motion of the intercalated dye molecules would be considerably impeded by the polymer, resulting in the enhancement of fluorescence.

We have also examined the effect of temperature on the fluorescence of julolidinemalononitrile (1) in poly(methyl methacrylate) films to probe the torsional relaxation processes of the various polymers over a wide temperature range. Figure 4 shows the temperature dependence of the fluorescence intensity, I_F, of 1 in isotactic PMMA. A remarkable resemblance of the I_F vs. T plot to the DSC thermogram of isotactic PMMA is observed; that is, a well-defined transition occurs at 43 °C. The temperature dependence of the fluorescence of 1 in syndiotactic or atactic PMMA[19] is somewhat different from that in isotactic PMMA. The fluorescence intensity of 1 in syndiotactic (or atactic)[19] PMMA decreases gradually with increasing temperature, as shown in Figure 5. A break in the I_F vs. T plot occurs at the glass transition temperature of the polymer, 125 °C for syndiotactic and 106 °C for atactic PMMA. The decrease in fluorescence of 1 in syndiotactic and atactic PMMA with increased temperature is due to increase in polymer chain motion creating sufficient free volume for the probe to rotate. Above the glass transition temperature significant segmental motion of the polymer chains occurs, permitting the probe to rotate freely. At such a point the fluorescence intensity levels off and approaches that in fluid media.

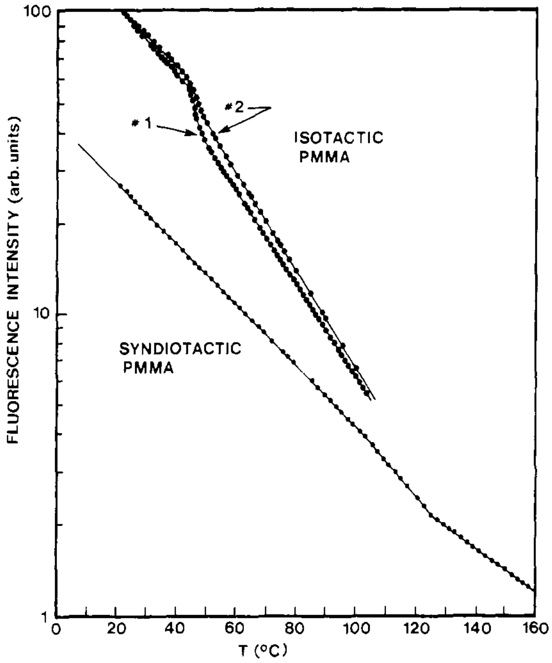


Figure 5. Effect of temperature on the fluorescence of 1 in syndiotactic and isotactic PMMA.

The fluorescence–temperature behavior of 1 in isotactic PMMA is radically different. A sharp drop in the fluorescence occurs at ~43 °C, followed by the normal decrease in I_F with increased temperature. This transition cannot be a glass transition but is rather consistent with a change in the conformation of the polymer chains from a tight, less flexible, to an open, more flexible, conformation.

The types of relaxation that take place in amorphous polymers in the temperature range of interest here are (1) localized main-chain motions involving the cooperative but restricted motion of segments of few contiguous monomer units (processes usually have activation energies in the neighborhood of 10 kcal/mol[29]) and (2) side-group motions such as methyl or ester groups, which tend to have smaller activation energies in the region of 2–4 kcal/mol. The activation energy for the relaxation process of isotactic PMMA at temperatures below 43 °C is 4.2 kcal/mol, consistent with side-group motion. Above 43 °C, the activation energy is 8.5 kcal/mol, which corresponds to localized main-chain motions.

On the basis of the above information, one must conclude that the conformational transition at 43 °C for isotactic PMMA is triggered by rotations of the side groups, which change the choice of the preferred conformation. Sundararajan,[13] on the basis of virtual bond analysis, suggested that the conformational transition at 43 °C corresponds to transition between 5(2) and 10(2) helices. The fluorescence results presented here are in full agreement with this model.

One final note on the apparent frequency independence of polymer transitions measured by the fluorescence technique is in order. For instance, the glass transition temperature determined by our probe (relaxation frequency 10^{11} Hz) agrees well with those determined by slow thermal relaxation techniques. The answer to this question lies in the fact that molecular and submolecular motions to which the probe is sensitive contribute to the macroscopic behavior of the polymer. In addition, the steady-state fluorescence measurements average out the macrodynamic behavior of the polymer chains.

Basically, two principal findings have emerged. One is the dependence of the fluorescence yield of molecular rotors on the tacticity of the polymer matrix. The other is the sensitivity of the fluorescence of molecular rotors to dynamic changes in the conformation of polymers over wide temperature ranges. One must remember that different relaxation techniques applied to polymeric materials respond with different sensitivity to the various types of molecular motion. The fluorescence probe method complements many of the well-established methods of polymer material research.

Acknowledgment. We are in debt to Drs. S. Sundararajan and T. Smith for many useful discussions.

Registry No. 1, 58293-56-4; atactic PMMA, 9011-14-7; isotactic PMMA, 25188-98-1.

References and Notes

(1) "Macromolecular Synthesis"; Overberger, C. G., Ed.; Wiley: New York, 1963; Vol. 1, p 29. Abe, H.; Imai, K.; Matsumoto, M. *J. Polym. Sci., Part C* **1968**, *23*, 469.

(2) Kawasaki, A.; Furukawa, J.; Tsuruta, T.; Inoue, S.; Ita, K. *Makromol. Chem.* **1960**, *36*, 260.

(3) Goode, W. E.; Owens, F. H.; Fellmann, R. P.; Synder, W. H.; Moore, J. E. *J. Polym. Sci.* **1960**, *56*, 317. Iwamoto, R.; Ohta, K.; Mimo, S. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 441.

(4) D'Alagni, M.; DeSantis, P.; Liquori, A. H.; Savino, M. *J. Polym. Sci., Part B* **1964**, *2*, 925.

(5) Fox, T. G.; Garrett, B. S.; Goode, W. E.; Gratch, S.; Kincaid, J. F.; Spell, A.; Stroupte, J. D. *J. Am. Chem. Soc.* **1958**, *80*, 1768.

(6) Shetter, J. A. *J. Polym. Sci., Part B* **1963**, 209.

(7) Steck, N. S. *SPE Trans.* **1964**, *4*, 1.

(8) Gall, W. A.; McCrum, N. G. *J. Polym. Sci.* **1961**, *50*, 489. Plazek, D. J.; Rahgupath, N. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1974**, *15*, 53.

(9) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173. Hatada, K.; Kitayama, T.; Okamoto, Y.; Ohta, K.; Umemura, Y.; Yuki, H. *Makromol. Chem.* **1978**, *179*, 485.

(10) D'Alagni, M.; DeSantis, P.; Liquori, A. M.; Savino, M. *J. Polym. Sci., Part B* **1964**, *2*, 925.

(11) Anzuno, Q.; Coiro, V. M.; D'Alagni, M.; DeSantis, P.; Liquori, A. M.; Savino, M. *Nature (London)* **1965**, *206*, 358.

(12) Kusanagi, H.; Tadokoro, H.; Chatani, Y. *Macromolecules* **1976**, *9*, 531.

(13) Sundararajan, P. R. *Macromolecules* **1979**, *12*, 575; "n_m represents the helix with n units in m turns".

(14) Beavan, S. S.; Hargreave, J. S.; Phillips, D. *Adv. Photochem.* **1979**, *11*, 207.

(15) Morawetz, H. *Science (Washington, D.C.)* **1979**, *203*, 405.

(16) Winnik, M. A.; Redpath, T.; Richard, D. H. *Macromolecules* **1980**, *13*, 328.

(17) Semerak, S. N.; Frank, C. W. *Macromolecules* **1981**, *14*, 443.

(18) Johnson, G. E.; Good, T. A. *Macromolecules*, submitted for publication.

(19) Loutfy, R. O.; Law, K. Y. *J. Phys. Chem.* **1980**, *84*, 2804; *Macromolecules* **1981**, *14*, 587. Loutfy, R. O. *Ibid.* **1981**, *14*, 270; *J. Polym. Sci.*, in press.

(20) Kuder, J. E.; Limburg, W. W.; Pochan, J. M.; Wychick, D. *J. Chem. Soc., Perkin Trans.* **1977**, *2*, 1643.

(21) Crescenzi, V.; D'Alagni, M.; Liquori, A. M.; Picozzi, L.; Savino, M. *Ric. Sci.* **1963**, *33 (II-A)*, 123.

(22) Goode, W. E.; Owens, F. H.; Fellmann, R. P.; Synder, W. H.; Moore, J. E. *J. Polym. Sci.* **1960**, *46*, 317.

(23) Goode, W. E.; Fellmann, R. P.; Owens, F. H. "Macromolecular Synthesis"; Wiley: New York, 1963; Vol. 1, p 25.

(24) Joh, Y.; Kotake, Y. *Macromolecules* **1970**, *3*, 337.

(25) Thompson, E. V. *J. Polym. Sci., Polym. Phys. Ed.* **1966**, *4*, 199.

(26) Melhuis, W. H. *J. Opt. Soc. Am.* **1964**, *54*, 183.

(27) Nishijima, Y. *J. Polym. Sci., Part C* **1971**, *31*, 353. Tredwell, C. J.; Osborne, A. D. *J. Chem. Soc., Faraday Trans. 2* **1980**, *12*, 1622. Taylor, J. R.; Adams, M. C.; Sibbett, W. *Appl. Phys.* **1980**, *102*, 847. Jarandias, J. *J. Photochem.* **1980**, *13*, 35. Karstens, T.; Koh, K. *J. Phys. Chem.* **1980**, *84*, 1871. Jones, G.; Jackson, W. R.; Halpern, A. M. *Chem. Phys. Lett.* **1980**, *72*, 391.

(28) Vitagliano, V.; Costantino, L.; Sartorio, R. *J. Phys. Chem.* **1976**, *80*, 959.

(29) Allan, S. In "Molecular Basis of Transitions and Relaxations"; Meier, D. J., Ed.; Gordon and Breach Science: London, 1978; p 20.

Effect of Different Shielding Groups on the Polyelectrolyte Behavior of Polyamines

R. Barbucci,* M. Casolaro, and N. Danzo

Istituto di Chimica Generale, 53100 Siena, Italy

V. Barone

Istituto Chimico, 80134 Napoli, Italy

P. Ferruti and A. Angeloni

Istituto di Chimica degli Intermedi, 40136 Bologna, Italy.

Received June 8, 1982

ABSTRACT: The stepwise protonation of three polymeric amines, containing a different shielding group between the amine moieties of the repeating units, has been studied from a thermodynamic standpoint. This was done for comparison purposes with structurally related poly(amido amines) whose monomeric units had been previously found to behave independently toward protonation. This study was performed by potentiometric and calorimetric techniques, and specific methods for the treatment of either "sharp" or "apparent" thermodynamic functions in polyelectrolyte having more than one basic group in the repeating unit have been developed.

Introduction

The thermodynamic functions for the protonation of polymeric bases usually depend on the degree of protonation of the macromolecule (i.e., on its total charge).[1] Up to now, in only two classes of polymers, poly(amido amines)[2] and poly(macrocycles),[3] have the monomeric units behaved independently toward protonation, thus giving rise to "sharp" thermodynamic functions.[4] ("Sharp" means that the thermodynamic functions do not depend on the degree of protonation (α) of the whole macromolecule, and "apparent" means that they do.)

In order to gain further insight into the structural reasons of this unusual trend, we have modified the monomeric units of poly(amido amines) in several respects[2,5-8]

0024-9297/83/2216-0456$01.50/0