Poly(methacrylic acid) Derivatives. 5. Microcalorimetric Study of Poly(*N*-methacryloyl-L-alanine) and Poly(*N*-methacryloyl-L-alanine-*co*-*N*-phenylmethacrylamide) in Aqueous Solutions

Michel Morcellet and Claude Loucheux

Laboratoire de Chimie Macromoléculaire (Equipe de Recherche Associée au CNRS No. 827), Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq, Cédex, France

Hubert Daoust*

Department of Chemistry, Université de Montréal, Montreal, Quebec, Canada H3C 3V1.
Received September 4, 1981

ABSTRACT: Heats of dilution and heats of dissociation of poly(*N*-methacryloylalanine) (PNMA), of poly(*N*-methacryloylalanine-*co*-*N*-phenylmethacrylamide) (P50), and of a model molecule, *N*-isobutyrylalanine (NPAIB), have been studied as a function of the degree of dissociation α by a microcalorimetric technique. For P50, which undergoes a conformational transition similar to that of poly(methacrylic acid) as α is increased, the thermodynamic parameters of the transition have been determined by a combined use of microcalorimetric and potentiometric data. The results show that the transition of P50 is essentially enthalpy driven, the enthalpy change during the transition being nearly equal to the heat of transfer of an aromatic ring from a nonpolar environment to water. The thermodynamic parameters of the dissociation of PNMA and P50 also emphasize the major role played by hydrophobic interactions.

Introduction

The knowledge of thermodynamic parameters of the conformational transition of polypeptides or synthetic polyelectrolytes is of great interest for the understanding of the mechanism of this transition. Especially, the microcalorimetric determination of the enthalpy of the conformational transition ΔH_t is of importance. The experimental method which is to be used depends on the nature of the polymer under study. For nonionizable polypeptides, two different methods can be used. If the helix → coil transition can be brought about by a change in temperature, then ΔH_t is determinable from measurements of the heat capacity at various temperatures through the transition region. Such experiments have been carried out for poly(ε-carbobenzoxy-L-lysine) (PCBL) in a mixture of dichloroacetic acid (DCA) and chloroform ($CHCl_3$),[1] for poly(γ-benzyl L-glutamate) (PBLG) in DCA and 1,2-dichloroethane (DCE),[2] and for PBLG in DCA–DCE mixtures.[3,4] If the helix cannot be melted thermally, it can usually be melted isothermally by a change in the composition of the solvent mixture. For example, ΔH_t has been determined for PBLG at 25 °C by varying the composition of mixtures of DCA and $CHCl_3$[5] and of DCA and DCE[6] and for PBLG, poly(γ-ethyl L-glutamate) (PELG), and poly(γ-methyl L-glutamate) (PMLG) at various temperatures by varying the composition of mixtures of DCA and DCE.[7-9]

For ionizable polypeptides, ΔH_t may be determined by changing the pH of the solution to induce the helix → coil transition. This process was used for poly(L-glutamic acid) (PLGA) in 0.1 N KCl at 30 °C,[10] for poly(L-lysine) (PLL) in 0.1 N KCl at various temperatures,[11] and for poly(L-ornithine) (PLO).[12] Another way is to add an organic solvent to an aqueous solution of the ionized coiled polymer in order to lower the dielectric constant and therefore to induce the transition to the helix. The enthalpy of the methanol-induced transition of PLL and PLO was obtained in this way.[13]

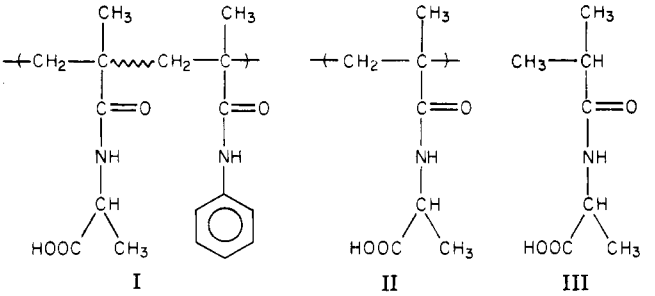
For synthetic polyelectrolytes such as poly(methacrylic acid) (PMA),[14,15] alternating copolymers of maleic acid and alkyl vinyl ethers (MA/RVE),[16,17] or alternating copolymers of maleic acid and styrene (MA/Sty),[18] the enthalpy ΔH_t of the conformational transition between the compact conformation and the coiled conformation can also be determined by varying the pH.

Recently, the synthesis of a series of hydrophilic–hydrophobic copolymers, poly[*N*-methacryloylalanine-*co*-*N*-phenylmethacrylamide] (I) (IUPAC nomenclature: poly-[1-[[(1-carboxyethyl)amino]carbonyl]-1-methylethylene-*co*-1-methyl-1-[(phenylamino)carbonyl]ethylene]), has been reported.[19]

These copolymers take up a compact conformation in water when they contain more than 15 mol % of the hydrophobic *N*-phenylmethacrylamide residue and undergo a compact conformation → coil transition when the pH is increased.

For each of these copolymers, the enthalpy of the conformational transition ΔH_t was deduced from the temperature dependence of the free enthalpy ΔG_t of the transition calculated from the potentiometric titration curves.[19-22] Unfortunately, this process is rather imprecise since it only gives a mean value of ΔH_t in the temperature range under study. This is very important when dealing with a transition driven by hydrophobic interactions because in such cases, ΔH_t strongly changes with temperature and can even change from negative to positive values.[16]

This paper reports the results of a direct calorimetric determination of the value of ΔH_t at 25 °C for a poly(*N*-methacryloylalanine-*co*-*N*-phenylmethacrylamide) containing 50 mol % of the hydrophobic residue. In addition, data concerning the heat of ionization and the heat of dilution of the homopolymer poly(*N*-methacryloylalanine) (PNMA) (II) and of the model molecule *N*-isobutyrylalanine (III) (NPAIB) are also presented.



I II III

Experimental Part

Samples. The synthesis of PNMA and of the copolymer has

0024-9297/82/2215-0890$01.25/0

been described elsewhere.[19] The copolymer sample used in this study contains 50 mol % of the hydrophobic residue and will be referred to hereafter as P50.

The PNMA sample has a weight-average molecular weight $M_w = (1.5 \pm 0.1) \times 10^5$ as determined by the approach to the sedimentation equilibrium technique as modified by Kleiner and Kegeles.[23]

The model molecule was prepared by the reaction of isobutyryl chloride with alanine. One mole of alanine was converted into the sodium salt by addition of 1 mol of sodium hydroxide and 200 mL of water and then cooled in ice. One mole of isobutyryl chloride and 1 mol of sodium hydroxide were added dropwise simultaneously under vigorous stirring. The mixture was acidified to pH 2 with HCl. Then, *N*-isobutyrylalanine was extracted and recrystallized from ethyl acetate; mp 155 °C. Isobutyric acid (Fisher Scientific Co., analytical grade) was used without further purification.

Aqueous solutions were prepared by direct dissolution of the samples in water except for P50, which was first converted to the sodium salt with sodium hydroxide and then passed through a cation exchange column in the H^+ form. Solutions prepared in this way were stable during many days, provided that they were kept in a refrigerator. The titer of the acid or polyacid solutions was determined by acid–base titration.

Potentiometric Titrations. Potentiometric titrations were performed at 25 °C with a Radiometer pH M64 pH meter following an experimental procedure already described.[19]

Viscosity Measurements. Viscosity measurements were performed at 25 ± 0.01 °C with a Fica Viscomatic automatic apparatus equipped with a modified Ubbelohde viscometer.

Microcalorimetric Experiments. These experiments were carried out at 25 °C with a Tian-Calvet differential microcalorimeter following a technique already described.[24]

In the experiments on the heat of protonation, one volume of the sample solution at a concentration of 2–3% by weight (polymer or small molecule) at a degree of neutralization α in water (adjusted with NaOH) and one volume of a HCl solution were placed in the two compartments of the mixing cell. (From the experimental point of view, it is more precise to record heats of protonation rather than heats of dissociation to avoid the contribution from the heat of formation of water (ΔH = 55.815 kJ·mol^{-1}),[25] which is 10–15 times larger than the mean heat of dissociation of our samples.)

Once the thermal equilibrium was attained, the cell was rotated, the solutions were mixed, and the heat effect was recorded. The amount of HCl in the cell was adjusted so that the change of the degree of neutralization α_1 to α_2 ($\Delta\alpha$) was not larger than 0.06 in each experiment. This procedure is essential because the heat of protonation (or dissociation) of a polyacid depends on its degree of dissociation. In addition, overall heats of protonation (from $\alpha_1 = 1$ to $\alpha_2 = 0$) were also recorded for the small molecules isobutyric acid and the model molecule NPAIB.

Separate dilution experiments were also carried out on the same sample solutions, replacing HCl solutions by water (1:1 dilutions). The results were used to correct the heat of protonation data for sample dilution effects. In a similar way the small corrections for the heat of dilution of HCl were also obtained, in good agreement with calculations based on the values of the National Bureau of Standards.[26]

In the following, results are presented as $\Delta H_{diss}(\bar{\alpha}) = f(\bar{\alpha})$, where $\bar{\alpha} = (\alpha_1 + \alpha_2)/2$ and $\Delta H_{diss}(\bar{\alpha})$ is the enthalpy of dissociation at a given $\bar{\alpha}$ value, calculated as

$$\Delta H_{diss}(\bar{\alpha}) = -(q - q_d^s - q_d^{HCl})/m \quad (1)$$

where q is the recorded heat effect obtained by adding m mol of HCl to a solution of the partially neutralized sample, q_d^s is the heat of dilution of the sample, and q_d^{HCl} is the heat of dilution of HCl.

The calorimeter was calibrated by the Joule effect and tested by measuring the heats of dilution of NaCl solutions, which were found to be in good agreement with literature values.[27] The validity of our experimental procedure was also established by measuring the heat of dissociation of isobutyric acid. Our experimental value was ΔH_{diss} = −4.115 kJ·mol^{-1} whereas the literature value is ΔH_{diss} = −4.226 kJ·mol^{-1}.[28,29]

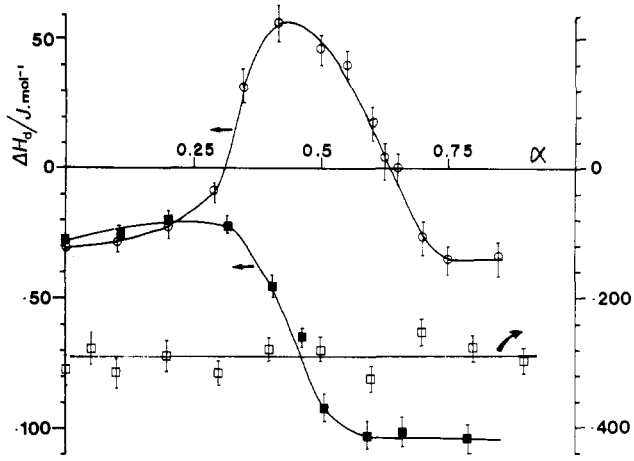


Figure 1. Variation of the heat of dilution ΔH_d vs. the degree of dissociation α for NPAIB (□), PNMA (■), and P50 (○).

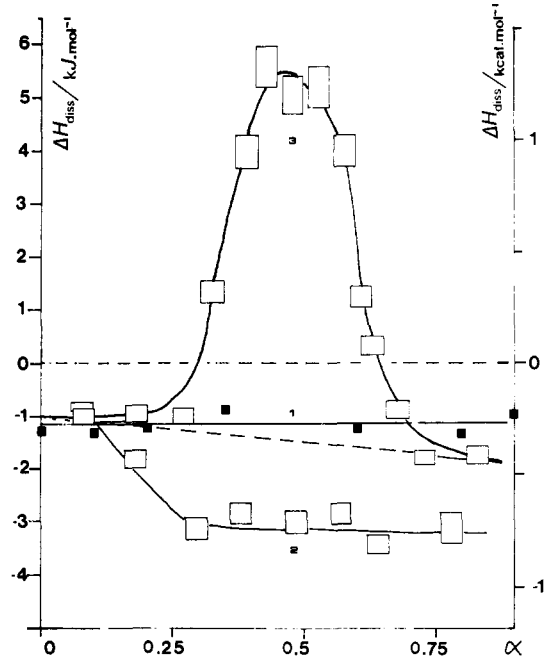


Figure 2. Variation of the heat of dissociation ΔH_{diss} vs. the degree of dissociation α for NPAIB (1), PNMA (2), and P50 (3).

Results and Discussion

Calorimetric data obtained with PNMA, P50, and NPAIB are reported in Figures 1 and 2. For NPAIB, the value of ΔH_d is independent of α, within experimental error. The mean value of ΔH_d for NPAIB is −290 ± 30 J·mol^{-1}.

For PNMA, the variation of ΔH_d with α is more complex: (a) ΔH_d is nearly constant between $\alpha = 0$ and $\alpha = 0.30$, decreases strongly between $\alpha = 0.30$ and $\alpha = 0.55$, and remains constant beyond $\alpha = 0.55$; (b) ΔH_d is always less negative than ΔH_d for the model molecule, which means that the dilution of the polymer is less exothermic than the dilution of the model molecule. Similar results were obtained with poly(acrylic acid), the dilution of which is less exothermic than the dilution of its model molecule, propionic acid.[24] This was explained by a chain effect associated with a change in the solvent structure: the dissolution of the polymeric chain in water requires the breaking of some water clusters, which is an endothermic process. The same explanation is probably valid also for PNMA. Since PNMA does not undergo any conformational transition upon dissociation of the carboxyl groups (increasing α), an explanation for the sudden decrease of

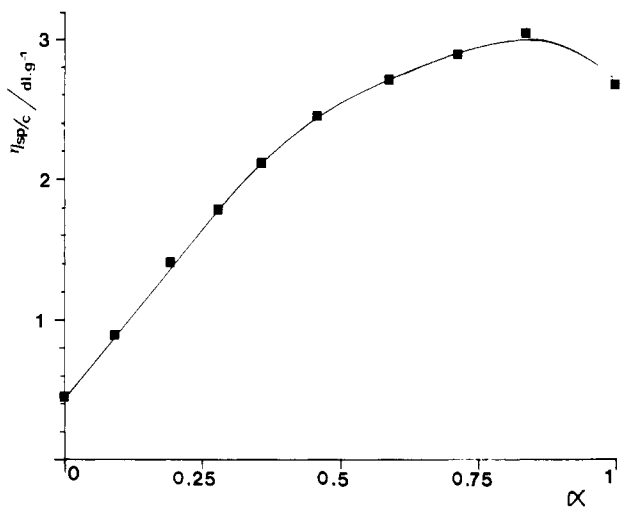


Figure 3. Variation of the viscosity vs. α for PNMA.

ΔH_d between $\alpha = 0.30$ and $\alpha = 0.55$ must be found elsewhere. Each repeating unit of PNMA contains an amide group and a carboxyl group. Thus the formation of hydrogen bonds is very likely to occur, especially when the polymer is in its un-ionized form. Upon dilution some hydrogen bonds are broken and this endothermic process could explain the rather low heat of dilution at $\alpha < 0.30$. At higher α values the hydrogen bonds involving the carboxyl group are already broken and dilution results in a more exothermic process. However, viscosity measurements (Figure 3) indicate no change in the hydrodynamic properties of PNMA upon ionization in the range α = 0.3–0.55.

Another explanation is based on Manning's theory, which predicts that the critical charge density for which the ion condensation behavior appears is $\alpha = 0.3$,[30] i.e., the value corresponding to the strong decrease in ΔH_d (Figure 1). Preliminary DC results indicate changes in intensity and wavelength of $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ amide group transitions for PNMA for α values between 0.3 and 0.5. So, the electrostatic interaction effect is noticeable. The results obtained with PNMA are also in good agreement with previous experimental findings that show that the dilution of poly(sodium acrylate) is more exothermic than the dilution of poly(acrylic acid) (PAA).[24] For P50 the variation of ΔH_d with α is quite anomalous (Figure 1). P50 exhibits an "endothermic peak" between $\alpha = 0.25$ and $\alpha = 0.75$, very similar to what was observed for poly(methacrylic acid) (PMA).[14] As with PMA, P50 undergoes, upon ionization, a conformational transition from a tightly coiled conformation (compact conformation), which exists at low α values, to a more expanded conformation, which exists at higher α values. From potentiometric titration experiments it has been shown that the conformational transition of P50 occurs between $\alpha = 0.25$ and $\alpha = 0.70$.[19] Thus, the "endothermic peak" in Figure 1 is related to the conformational transition in which the hydrophobic groups of P50, buried inside the compact conformation, become exposed to water molecules upon ionization.

In the whole range of α values, the heats of dilution of P50 are greater than those of PNMA; similar results have been obtained for PMA and PAA.[14]

As expected for a small molecule, the heat of dissociation of NPAIB is independent of the average degree of dissociation, as shown in Figure 2. Partial protonation experiments ($\Delta\alpha \leq 0.06$) give $\Delta H_{diss} = -1160 \pm 230$ J·mol^{-1} whereas overall protonation experiments ($\Delta\alpha \sim 0.95$) give $\Delta H_{diss} = -1310 \pm 20$ J·mol^{-1}).

For PNMA and P50, ΔH_{diss} depends on α. For PNMA the difference between ΔH_{diss} and $\Delta H°_{diss}$ (the extrapolated value for $\alpha = 0$) becomes more negative with increasing α (excess enthalpy of dissociation). At $\alpha = 0$, $\Delta H°_{diss}$ is nearly equal to the value obtained for the model molecule. This behavior is very similar to that of PAA and other poly(carboxylic acids)[31,32] and to that of di- and tricarboxylic acids, for which the enthalpy of the dissociation of the second and third carboxylic group is more negative than that of the first one.[33,34] After a rapid decrease between $\alpha = 0$ and $\alpha = 0.3$, ΔH_{diss} remains nearly constant up to $\alpha = 0.8$. The break at $\alpha = 0.3$ has also been observed in the variation of ΔH_{diss} for PAA[31,32] and has been theoretically predicted and attributed to ion condensation.[32] For PAA the excess enthalpy of dissociation at high α values is about −4.6 kJ·mol^{-1},[14,31,32] against −1.88 kJ·mol^{-1} for PNMA. This is explained by the longer side chains of PNMA, which induce a decrease in the electrostatic interactions between the carboxylate groups compared to PAA. The variation of ΔH_{diss} vs. α for P50 is very different from that observed for PNMA. Between $\alpha = 0.25$ and $\alpha = 0.70$ and "endothermic peak" is observed in the domain corresponding to the conformational transition and is very similar to the variation of the heat of dilution of P50 (Figure 1). This effect is very important since the heat of dissociation is positive between $\alpha = 0.3$ and $\alpha = 0.6$ whereas the heat of dissociation of PNMA is always negative. By analogy with the treatment of potentiometric titration data which allow the determination of the free enthalpy ΔG_t of the conformational transition,[14,19] the (hypothetical) variation of ΔH_{diss} in the absence of the conformational transition is represented by the interpolated base line between $\alpha = 0.25$ and $\alpha = 0.75$. The excess heat of dissociation compared to this base line is attributed to the heat of the conformation transition ΔH_t, i.e., the nonelectrostatic part of the charging process of P50.[14] Using the independent experimental values of ΔH_t and ΔG_t, one can obtain a complete thermodynamic characterization of the transition of P50, including the corresponding entropy change ΔS_t, from

$$\Delta G_t = \Delta H_t - T\Delta S_t \qquad (2)$$

The accuracy in the determination of ΔH_t depends, of course, on the uncertainty in the ΔH_{diss} values but also depends on the change in the α value ($\Delta\alpha$) during a protonation experiment. This is taken into account in Figure 2, where error area represents both kinds of errors. The relative errors on ΔH_{diss} range from ±6% to ±15%, depending on the magnitude of the heat effect (see Figure 2). Following this, the experimental value of ΔH_t is estimated to 1925 ± 300 J·mol^{-1}. The uncertainty on ΔH_t is thus ±15% whereas a 5% uncertainty has been reported for PMA in a previous work.[14] The free enthalpy of transition ΔG_t is derived from potentiometric titration curves, $pK_{app} = pH - \log\{\alpha/(1-\alpha)\}$ vs. α (Figure 4), according to a process previously described.[19,20] The value obtained is $\Delta G_t = 2050 \pm 125$ J·mol^{-1}.

Combination of ΔG_t and ΔH_t according to eq 2 gives for the entropy change $\Delta S_t = -0.42 \pm 1.26$ J·K^{-1}·mol^{-1}. For the lower copolymers in the series of P50 (P38 and P24) the ΔS_t value deduced from the temperature dependence of ΔG_t[19] is $\Delta S_t = 0$, in good agreement with the present results. For PMA, the ΔS_t value in water is positive:[14,35] $\Delta S_t = 0.71 \pm 0.44$ J·K^{-1}·mol^{-1}. Thus, the value found for P50 seems lower, despite experimental errors. This could be due to an increased entropy of the initial state (compact conformation) compared to PMA or to a decreased entropy of the final state, which is, we believe, the major factor responsible for the decrease in ΔS_t. Upon conformational

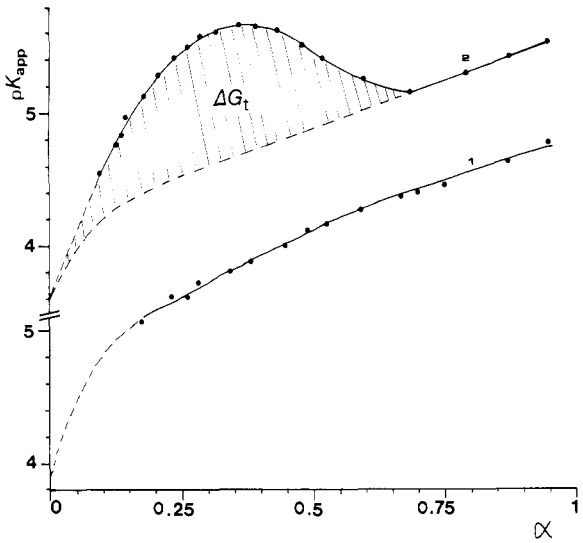


Figure 4. Variation of the apparent dissociation constant pK_{app} vs. α for PNMA (1) and P50 (2).

transition, the hydrophobic groups of P50 are exposed to water and reinforce thus its structuration. Comparison of the ΔH_t value found for P50 with previous values found for the lower copolymers (P38 and P24)[19] indicates that the enthalpy of transition in this series increases linearly with the amount of hydrophobic residues. The comparison with literature data concerning the enthalpy of transfer of a hydrophobic residue from a nonpolar environment to water is also of interest. Okuda et al. have studied the conformational transition of an alternating (50/50) copolymer of maleic acid and styrene.[18] In this case, ΔH_t = 1614 J·mol^{-1} at 25 °C. Besides, the heat of transfer of a benzene molecule to an aqueous medium is about 2100 J·mol^{-1} at 25 °C,[36] which coincides with the present value of ΔH_t for P50 (which contains one hydrophobic side chain for each ionizable side chain). Thus the ΔH_t value of P50 must be attributed mainly to the change in the environment of the *N*-phenylmethacrylamide side chains upon the conformational change. A similar comparison has been made between the ΔH_t value of a maleic acid–*n*-butyl vinyl ether copolymer and the heat of transfer of leucine and isoleucine.[37]

The comparison between potentiometric and calorimetric data also gives information on the variation of the entropy of dissociation ΔS_{diss} with α. Figure 4 gives the variation of pK_{app} vs. α for PNMA and P50. For each α value, the free enthalpy of dissociation ΔG_{diss} can be calculated according to

$$\Delta G_{diss} = 2.303RT(pK_{app}) \quad (3)$$

and then the value of ΔS_{diss} is obtained by

$$\Delta S_{diss} = (\Delta H_{diss} - \Delta G_{diss})/T$$

On Figure 5 the variation of ΔS_{diss} vs. α is also reported for PAA[31] for comparison. The entropy of dissociation is less negative for PNMA than for PAA. This indicates a weaker water immobilization during the charging process of PNMA compared to PAA. This is probably related to a lower charge density due to longer side chains.

At $\alpha < 0.3$ the variation of ΔS_{diss} for P50 is very close to that of PNMA. This means that in the compact conformation most of the hydrophobic groups are screened from contact with water. Between $\alpha = 0.3$ and $\alpha = 0.50$, $-\Delta S_{diss}$ suddenly decreases. This indicates a decrease in water immobilization, probably due to a change in the local dielectric constant and to a restructuration of the solvent

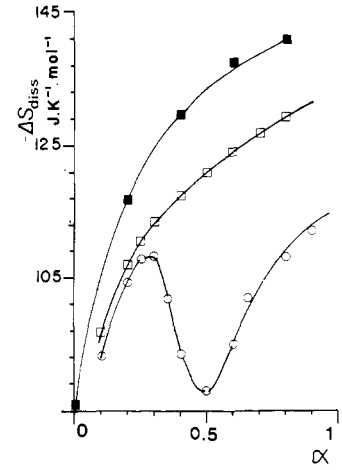


Figure 5. Variation of the dissociation entropy change ΔS_{diss} vs. α for PAA (■),[31] PNMA (□), and P50 (○).

surrounding the macromolecule occurring during the conformational transition. After $\alpha = 0.5$, $-\Delta S_{diss}$ increases again upon charging the molecule. At high α values, $-\Delta S_{diss}$ is much smaller for P50 than for PAA. This is in agreement with results obtained with other hydrophilic–hydrophobic copolymers[31] and must be related to the presence of the hydrophobic groups.

These results emphasize the role played by hydrophobic interactions in the variation of the entropy during the charging process (ΔS_{diss}) and during the conformation transition (ΔS_t). The value found for ΔH_t is in good agreement with other available data and indicates that the compact-to-coil transition of P50 depends mainly on the enthalpy term. It also appears that more data should be accumulated about the heat of dilution of PNMA (intermediate heats of dilutions as a function of concentration) to have a better understanding of the changes occurring between $\alpha = 0.3$ and $\alpha = 0.5$.

Acknowledgment. The assistance of Dr. Joëlle Morcellet-Sauvage and Dr. Nga Hoduc in the realization of some parts of this work is gratefully acknowledged. This work has been made possible thanks to a NATO fellowship to M.M. and to the Natural Sciences and Engineering Research Council of Canada.

References and Notes

(1) Karasz, F. E.; O'Reilly, J. M.; Bair, H. E. *Biopolymers* **1965**, *3*, 241.
(2) Karasz, F. E.; O'Reilly, J. M.; Bair, H. E. *Nature (London)* **1964**, *202*, 693.
(3) Ackermann, T.; Ruterjans, H. *Z. Phys. Chem. (Wiesbaden)* **1964**, *41*, 116.
(4) Ackermann, T.; Neumann, E. *Biopolymers* **1967**, *5*, 649.
(5) Kagemoto, A.; Fujishiro, R. *Makromol. Chem.* **1968**, *114*, 139.
(6) Kagemoto, A.; Fujishiro, R. *Biopolymers* **1968**, *6*, 1753.
(7) Daoust, H.; Choquette, M.; Hoduc, N. *Biopolymers* **1976**, *15*, 2059.
(8) Giacometti, G.; Turola, A. *Z. Phys. Chem. (Wiesbaden)* **1966**, *51*, 108.
(9) Giacometti, G.; Turola, A.; Boni, R. *Biopolymers* **1968**, *6*, 441.
(10) Rialdi, G.; Hermans, J., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 5719.
(11) Chou, P. Y.; Scheraga, H. A. *Biopolymers* **1971**, *10*, 657.
(12) Chang Fu, Y.; Vanwart, H. E.; Scheraga, H. A. *Biopolymers* **1976**, *15*, 1795.
(13) Baba, Y.; Kagemoto, A.; Fujishiro, R. *Makromol. Chem.* **1979**, *180*, 2221.
(14) Crescenzi, V.; Quadrifoglio, F.; Delben, F. *J. Polym. Sci., Part A-2* **1972**, *10*, 357.
(15) Delben, F.; Crescenzi, V.; Quadrifoglio, F. *Eur. Polym. J.* **1972**, *8*, 933.
(16) Crescenzi, V.; Quadrifoglio, F.; Delben, F. *J. Polym. Sci., Part C* **1972**, *39*, 241.
(17) Martin, P. J.; Morss, L. R.; Strauss, U. P. *J. Phys. Chem.* **1980**, *84*, 577.

(18) Okuda, T.; Ohno, N.; Nitta, K.; Sugai, S. *J. Polym. Sci., Part A-2* **1977**, *15*, 749.
(19) Morcellet-Sauvage, J.; Morcellet, M.; Loucheux, C. *Makromol. Chem.* **1981**, *182*, 949.
(20) Morcellet-Sauvage, J.; Morcellet, M.; Loucheux, C. *Makromol. Chem.*, in press.
(21) Wada, A. *Mol. Phys.* **1960**, *3*, 409.
(22) Leyte, J. C.; Mandel, M. *J. Polym. Sci., Part A-2* **1964**, *2*, 1879.
(23) Kleiner, S. M.; Kegeles, G. *J. Phys. Chem.* **1955**, *59*, 952.
(24) Cartier, J. P.; Daoust, H. *Can. J. Chem.* **1971**, *49*, 3935.
(25) Olofsson, G.; Hepler, L. G. *J. Solution Chem.* **1975**, *4*, 127.
(26) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schuum, R. H. *NBS Tech. Note* **1968**, *No. 270-3*, 27.
(27) Fortier, J. L.; Leduc, P. A.; Picker, P.; Desnoyers, J. E. *J. Solution Chem.* **1973**, *2*, 467.
(28) Eberson, L.; Wadso, I. *Acta Chem. Scand.* **1963**, *17*, 1552.
(29) Canady, W. J.; Papee, H. M.; Laidler, K. J. *Trans. Faraday Soc.* **1958**, *54*, 502.
(30) Manning, G. S. *Annu. Rev. Phys. Chem.* **1972**, *23*, 117.
(31) Crescenzi, V.; Delben, F.; Quadrifoglio, F.; Dolar, D. *J. Phys. Chem.* **1973**, *77*, 539.
(32) Gunnarsson, G.; Wennerstrom, H.; Olofsson, G.; Zacharov, A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1287.
(33) Ives, D. J. G.; Prasad, D. *J. Chem. Soc. B* **1970**, 1652.
(34) Larson, J. W.; Hepler, L. G. In "Solute-Solvent Interactions"; Marcel Dekker: New York, London, 1969; pp 1-44.
(35) Nekrasova, T. N.; Gabrielyan, A. B.; Ptitsyn, O. B. *Polym. Sci. USSR (Engl. Transl.)* **1968**, *10*, 348.
(36) Bohon, R. L.; Claussen, W. F. *J. Am. Chem. Soc.* **1951**, *73*, 1571.
(37) Dubin, P.; Strauss, U. P. *J. Phys. Chem.* **1967**, *71*, 2757.

Photochemical Reaction of Nitrosyl Chloride with Polyethylene

James F. Kinstle* and Stuart L. Watson

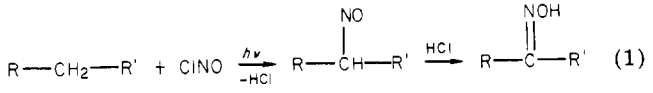
Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37919.
Received September 4, 1981

ABSTRACT: Irradiation of NOCl with low molecular weight alkanes yields oximes after rearrangement of the intermediate nitroso group. Upon irradiation of NOCl with high-density polyethylene, the oxime was not observed, but *gem*-chloronitroso and nitrato functionalities were found. The *gem*-chloronitroso group was proposed to arise from reaction of NOCl with the oxime, while the nitrate was proposed to originate from reaction of NO with the intermediate nitroso functionality. Possible mechanistic pathways to these products are discussed.

Introduction

Polymeric materials have found application in many areas as structural or decorative devices. Often the bulk properties of the polymer match the requirements for a given application, while the surface region is lacking in some critical property such as wettability. An example of a polymer having such characteristics is PE (polyethylene), which has interesting bulk properties useful in many ways, yet has surface characteristics which generally yield poor adhesion. This problem has been addressed often and successfully by techniques such as oxidative surface modification and by grafting. Our interest in modifying PE has recently been in the area of photochemically induced reactions.

In his pioneering work, Lynn[1] found that photoreaction of NOCl (nitrosyl chloride) with low molecular weight alkanes yields oximes. The pathway for this reaction apparently proceeds through the nitroso group, which then rearranges to the oxime:



(1)

Müller[2] later developed the reaction quite extensively, eventually revealing an efficient synthesis of cyclohexanone oxime from cyclohexane.

As a part of our continuing interest in photochemical modifications of polymers,[3] this reaction appeared to be a route to the formation of carbon–nitrogen bonds on PE (polyethylene),[4] particularly HDPE (high-density PE). Our initial results indicated that the reaction pathway differed from that observed with low molecular weight alkanes, which prompted the detailed study described in this report.

While our work was in progress, two other groups reported on their work involving the photoreaction of NOCl with PE. Pozzi et al.[5a] attempted to use the reaction to form oximes on the polymer followed by a hydrolysis procedure to transform the oxime group to a carbonyl functionality to yield a photodegradable polymer. Degtyareva et al.[5b] reported an infrared spectrophotometric investigation of the products of the photoreaction of NOCl with PE and observed the presence of the oxime along with a *gem*-chloronitroso functionality and chlorinated hydrocarbon. Our results differed from these reports, and the differences are detailed in the Discussion.

Experimental Section

The HDPE film utilized had a thickness of approximately 0.038 mm (1.5 mil) and was specially prepared from Phillips Marlex 6006. This material is reported to be a linear polyethylene with a moderately broad molecular weight distribution. The measured density was 0.955 g cm^{-3} at 25 °C, and the crystallinity was calculated to be 71%. For experiments conducted with LDPE (low-density PE) a commercial film of thickness 0.032 mm (1.25 mil) was employed. All gases, Cl_2, HCl, NO, NO_2, and NOCl, were received from Matheson, fractionally distilled three times, and stored over phosphorus pentoxide.

Photolyses were performed in a cylindrical cell, 4.3 cm o.d. × 31 cm, constructed of Pyrex, in which the PE film was supported on a cylindrical Pyrex insert, 2.8 cm o.d. and 19 cm in length. All work with the gases was conducted on a standard vacuum assembly with illumination by a Kodak Safelight. All irradiations were carried out in a Rayonet Type RS preparative photochemical reactor from Southern New England Ultraviolet Co. equipped with four 12.5-W RUL 3500A lamps.

Infrared spectra were determined with a Beckman IR5A spectrophotometer and a Digilab FTS-20 Fourier transform infrared spectrometer. Mass spectra were accomplished with a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Results

A series of photolyses was carried out by using different gases with HDPE. The residual gases were analyzed by mass spectroscopy, and the films were analyzed by infrared

0024-9297/82/2215-0894$01.25/0