Thermochimica Acta, 117 (1987) 37–43
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DETERMINATION OF RESIDUAL UNSATURATION IN POLYENE PREPARATIONS BY DIRECT INJECTION ENTHALPIMETRY

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(Received 11 November 1986)

ABSTRACT

Direct injection enthalpimetric methods for the determination of residual unsaturation in both water and hydrocarbon soluble polymers are described. Both methods are based on the heat of bromination of double bonds. The method for water-soluble polymers is a new method, while the method described for hydrocarbon-soluble polymers is a modification of literature methods which makes these previous methods simpler and quicker to use.

INTRODUCTION

The residual unsaturation, remaining either as unreacted monomer or as end groups, in a polyene preparation has significant effects on the properties of the preparation. The stability to light, oxidation, and temperature as well as the biological toxicity of the polymer preparation are often determined by the amount of unsaturation present. For example, the stability of synthetic oils and rubbers prepared from olefins is related to the total unsaturation remaining in the final product, and the toxicity of polyacrylate preparations depends on the amount of monomer left in the final product.

The concentration of carbon–carbon double bonds in oils and rubbers has usually been determined by hydrogenation or halogenation. Thermometric, coulometric, potentiometric, and back-titration methods have all been used to follow the course of or to locate the endpoint of the reaction [1]. Methods for the determination of residual unsaturation in polyacrylates have concentrated instead on methods for separating and determining the residual monomer [2–4]. A kinetic method based on the reaction of the acrylate carbon–carbon double bond with n-laurlymercaptan has also been published [5].

This paper reports a new procedure for the determination of residual unsaturation in aqueous emulsions of polyacrylates and a simplified procedure for the determination of unsaturation in oils and rubbers. Both procedures are based on the reaction of bromine with carbon–carbon double bonds and the measurement of the accompanying temperature rise.

0040-6031/87/$03.50

EXPERIMENTAL

Reagents

All chemicals used were reagent grade or better. Commercial samples of acrylamide/acrylic acid copolymers (sample A was an 80/20 copolymer and sample B was a 70/30 copolymer) and synthetic rubbers and oils were used to test the procedures.

Equipment

A Tronac model 450 isoperibol titration calorimeter [6] equipped with a 25 ml Dewar, a 10 ml motorized buret delivering 1 ml min^{-1}, and a Hewlett-Packard recorder model 7100B was used to collect the direct injection enthalpimetric data in this report. The water bath of the calorimeter was controlled at 298 K. The thermistor bridge had a sensitivity of about 20 mV K^{-1} and the thermal equivalent of the calorimeter was 4.90 ± 0.04 J mV^{-1} when the Dewar was filled with the aqueous polymer solution. Because of the viscosity of the aqueous polymer solutions, the thin-bladed stirrer normally supplied with the calorimeter did not give adequate mixing and was replaced with a stirrer with hemispherical, 45° angled blades. The stirrer was driven at 800 rpm in the direction of rotation so as to push down on the solution. If the stirrer was driven in the normal direction, i.e. so that it lifted the solution, the aqueous polymers tended to wind onto the stirrer shaft and rise into the bearing. The recorder was operated at 0.5, 1, 5 or 10 mV full scale as appropriate and at 0.5 in. min^{-1}.

A Carlo-Erba gas chromatograph with an on-column injector, an FID detector, and a 12 m × 0.31 mm fused silica capillary column with SE-52 bonded phase coating was used to determine the concentration of monomers present in the acrylate polymers. Hydrogen at 100 cm sec^{-1} was the carrier gas. The sample was trapped in a cryogenic trap with dry ice after which the oven was programmed from 20 to 40°C at 4°C min^{-1}.

Extraction and gas chromatographic procedure for determination of acrylamide and acrylic acid in aqueous polyacrylate solutions

A 40 g sample of 1% polyacrylate solution was acidified to a pH between 1 and 2 with HCl, extracted with two 100 ml portions of dichloromethane by vigorously stirring for two hours with each portion, the dichloromethane extracts were combined, and evaporated to 0.2–0.3 ml under a stream of nitrogen. Aliquots (0.4 μl) of the resulting concentrate were injected into the gas chromatograph. Retention times for acrylamide and acrylic acid were verified both by co-injection of standards and from the mass spectra of the peaks.

Direct injection enthalpimetric procedure for aqueous polyacrylate solutions

The titrant was prepared by saturating a solution of equal volumes of 2M NaCl and water with bromine. The final concentration of NaCl matched that in the polymer solutions. The polyacrylamide solutions were diluted with water and 2M NaCl so that the final concentration of polyacrylamide was less than 0.07% and the NaCl was 1 M. Twenty to 22 g of this solution was weighed into the Dewar, 0.5 ml of 1 M HCl was added, the Dewar was placed on the calorimeter, the temperature was brought to bath temperature, and 1 ml of titrant was injected with the buret. The chart was allowed to run until a straight line with a slope less than the lead was obtained for about 15 min. A blank was determined for each determination by cooling the Dewar back below bath temperature and repeating the injection of bromine. Figure 1 shows the form of the data obtained and the method of data analysis.

Direct injection enthalpimetric procedure for cyclohexane solutions of oils and rubbers

In this procedure a bromine solution in cyclohexane was used as the titrate and the oil solution to be analyzed was injected into the bromine solution. A 20 ml aliquot of the cyclohexane solution of bromine (~ 5% by weight) was placed in the Dewar, the temperature of the solution in the Dewar was brought to bath temperature, and 1 ml of the cyclohexane solution of the oil or rubber containing 40 to 100 μmol of carbon–carbon double bonds was injected. The chart was allowed to run until a straight line was obtained for about 15 min. The data were analyzed as shown in Fig. 1. Several injections were made before the bromine solution was replaced. A

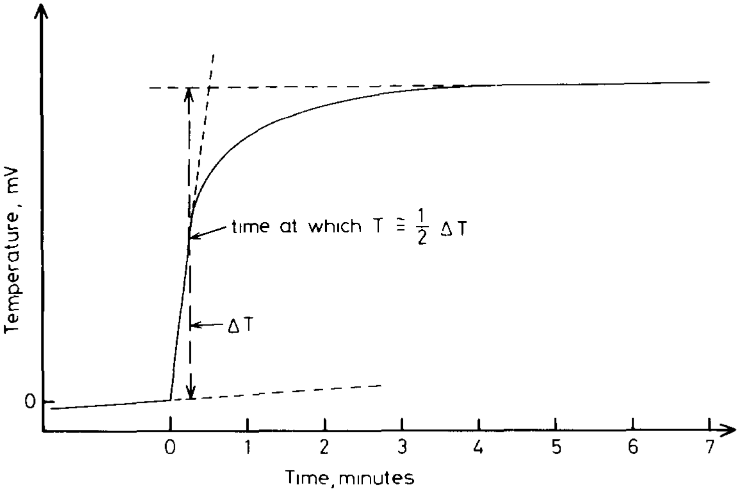

Fig. 1. Schematic diagram of the calorimeter output and the method of data analysis.

correction was made for the change in the thermal equivalent of the calorimeter on each addition.

RESULTS

The results obtained for the determinations of unsaturation in the polyacrylate samples by the calorimetric procedure and by GC are given in Table 1.

The results obtained with standard solutions of acrylamide and acrylic acid are shown in Fig. 2.

Except for the data obtained in the polymer solutions, the data shown in Fig. 2 are not corrected for the blank in order to emphasize the variation in the intercept. The intercepts are different for different NaCl solutions even though the solutions were prepared in supposedly identical ways. We attribute this variation in the intercept or blank value to slight mismatches in the concentrations of NaCl in the titrant and titrate which were prepared at different times. The problem is not a serious one since the intercept of the calibration line for given titrant and titrate solutions is accurately determined during the blank injection following the reaction injection. The blank done in the presence of polymer would not necessarily be expected to be the same as that in just NaCl because the heat of dilution would be different. The intercept of the calibration line with polymer present as shown in Fig. 2 is very different from zero because of the residual monomer present in the polymer as received. The blanks determined in the actual polymer solutions used in this study were zero.

The slopes of the calibration lines are directly related to the enthalpy change for the reaction of the compound with bromine. The slopes of the

TABLE 1

Residual unsaturation in polymers as measured by different methods

Sample	Unsaturation (nmol g^{-1} of polymer) [a]	
	by DIE	by GC or iodine number
Polyacrylate-A	488 ± 85	917 ± 455 (689, acrylamide; 228, acrylic acid) [b]
Polyacrylate-B	384 ± 91	884 ± 390 (598, acrylamide; 286, acrylic acid) [b]
Synthetic oil	336 ± 18	80 ± 40 [c]
Synthetic rubber	2130 ± 60	740 ± 80 [c]

[a] Uncertainties are expressed as the deviation of duplicate measurements.

[b] Measured by extraction and gas chromatography as described in the text.

[c] Calculated from the iodine number supplied by the manufacturer.

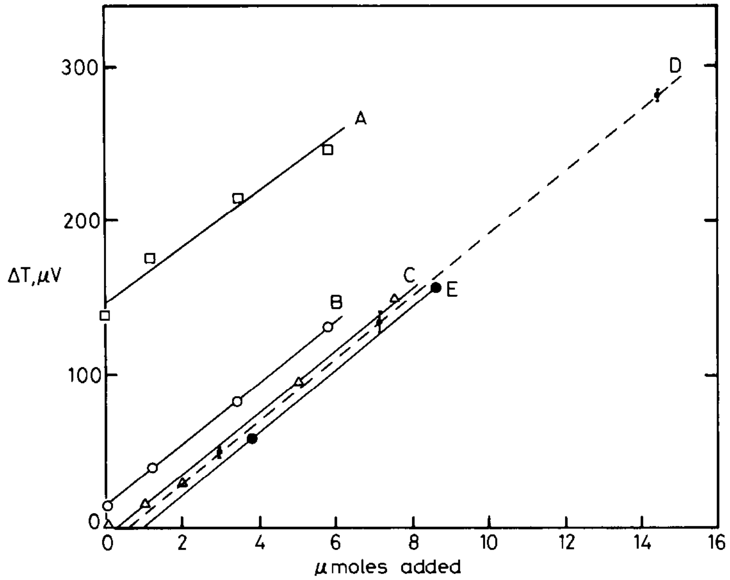

Fig. 2. Calibration data with acrylamide and acrylic acid. The data on lines B, D and E are for acrylamide dissolved in 1 M NaCl. The data on line C are for acrylic acid dissolved in different, but all nominally 1 M NaCl, solutions. The data on line A are for acrylamide dissolved in a solution which is 0.071% by weight acrylamide/acrylic acid copolymer and 1 M NaCl. The equations of the linear least square lines shown are (A) $\Delta T = +(147 \pm 7) + (18.3 \pm 2.0)n$, (B) $\Delta T = +(14 \pm 2) + (20.2 \pm 0.6)n$, (C) $\Delta T = -(5 \pm 4) + (20.3 \pm 1.0)n$, (D) $\Delta T = -(12 \pm 1) + (20.4 \pm 0.1)n$, and (E) $\Delta T = -21 + 20.7n$ where n is the number of μmol of acrylate added and ΔT is in μV. The points shown represent individual data points, except line D where the points shown are averages of three measurements. The error bars on the points on line D give the standard deviation around each point. Only the data for line A are blank corrected.

calibration lines obtained with each of the different acrylate preparations are the same within experimental error. A significant point to note is that acrylamide and acrylic acid gave the same calibration slope. Also, the presence of the polymer apparently does not affect the slope of the calibration line.

TABLE 2

Results of calibration runs with cyclohexene [a]

Cyclohexene taken (μmol)	Temperature rise (mV)	Mean	Std. Dev.
34.6	1.79, 1.91, 2.14	1.95	±0.10 (5%)
41.2	2.30, 2.59, 2.65	2.51	±0.11 (4%)
53.3	2.88, 3.29, 3,58	3.25	±0.20 (6%)
56.0	3.21, 3.31, 3.47, 3.47, 3.56, 3.64, 3.78	3.49	±0.07 (2%)
107.3	5.65, 6.23, 6.70, 6.90	6.37	±0.28 (4%)

[a] A linear least squares fit of all the data shown gives $n(\mu\text{mol}) = (1 \pm 3) + (16.3 \pm 0.8) \times$ temperature rise.

A comparison of the results obtained on the commercial samples by direct injection enthalpimetry and by iodine number is given in Table 1.

The results obtained with standard solutions of cyclohexene in cyclohexane are given in Table 2. The scatter of these data is much greater than the scatter of the data obtained for the acrylates (see Fig. 2). We feel this is due to the greater difficulty in quantitative handling of the oxygen and light-sensitive nonaqueous solutions as compared to the aqueous solutions which are not sensitive to air and light. Also, we were unable to extend the determination to lower concentrations of cyclohexene because of significant positive deviations which appeared when the amount of cyclohexene was less than 30 μmol. As also shown in Table 2, the relative scatter was about the same at all of the cyclohexene concentrations used.

DISCUSSION

The direct injection enthalpimetric results on the acrylates are lower than, but within, the range of the results obtained by extraction and gas chromatography (see Table 1). Considering the difficulties in quantitating the gas chromatography results, we believe the results are in reasonable agreement.

The method for determining residual unsaturation in water-soluble polymers as reported here is significantly faster, simpler, and more precise than the extraction–gas chromatography procedure. The detection limit is low enough for the method to be useful for monitoring polymer preparations for toxicity in environmental or biological applications.

Previously developed thermometric methods for determination of unsaturation in materials soluble in non-polar solvents have either injected the halogenating reagent into the unknown [1] or have injected the unknown into a catalyst slurry for hydrogenation [6]. Injecting the unknown into a reaction medium has the advantage that several samples can be done before the calorimeter need be disassembled and the reagent replaced. Hydrogenation is, however, more complex because of the need to handle both a poison-sensitive catalyst and a gas. The procedure described here uses the best features of both of these previous methods by injecting the unknown into a reactant medium which is simple to prepare and use.

The choice of a standard for a given determination will depend on the actual structure of the unsaturated molecule. We have chosen cyclohexene as a convenient, representative olefin in this work and have then used the cyclohexene calibration to calculate the concentration of olefin in the oils and rubbers since the heat of bromination of olefins does not vary greatly with structure [1].

The enthalpimetric method gave significantly higher results on the commercial samples than were reported by the manufacturer as determined by reaction with iodine. We believe our results to be more accurate. Iodine numbers tend to be low because of the low reactivity of iodine towards hindered double bonds. The reaction of bromine which we have used would give high results only if the bromine reacted with some part of the polymer other than the double bond. We do not believe this occurs to a significant extent in the short reaction times used with the bromine. The most reactive site in the polymer (other than residual double bonds) is the tertiary carbon C–H which can undergo substitution by bromine. The substitution reaction is significantly slower than the bromination of double bonds, such that we would expect to see the heat from this reaction occurring during the trail period of the thermogram (see Fig. 1). There is no evidence in the thermograms for such a slow reaction. Thus, we conclude that the substitution reactions of bromine are not occurring under the conditions and time scale of the double bond determination.

ACKNOWLEDGMENTS

The authors thank Mr D.W. Later for doing the extraction–gas chromatography experiments and Mr Larry Dungan for performing the calorimetric measurements. LDH thanks St. Francis Xavier University for the award of the W.F. James Chair of Pure and Applied Science which provided the time to prepare this work for publication.

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