JOURNAL OF MATERIALS SCIENCE **34** (1999) 2135–2137

Hydrogen bonding in poly(styrene-mono-ethyl-maleate)

C. ANDREI, G. MOISE
Chemical Technology Institute Brazi, Uzinei Str., no. 1, Brazi 2011, Romania

This paper studies the styrene-(mono-ethyl-maleate) copolymer using IR spectroscopy. The copolymer was obtained by styrene copolymerization with maleic anhydride, in ethanol as the reaction medium. The IR spectra recorded give information concerning the physico-chemical structure, the monomer ratio and emphasize the intermolecular interactions corresponding to the hydrogen bond associations. The elevated temperature studies (90–130 °C) allowed us to establish the equilibrium constants, the enthalphy and entropy variation, values of -4.2 kcal mol^{-1} and -3.7 e.u. mol^{-1}, respectively, being obtained. © *1999 Kluwer Academic Publishers*

1. Introduction

Because of the present tendency of obtaining new materials applicable in various fields great interest is given to the synthesis of polymers with polar functional groups. The presence of polar groups in macromolecules determines the appearance of dipole-dipole interactions, hydrogen bonds and induction effects. These interactions have great importance in obtaining homogeneous polymer mixtures. In high-molecular systems which contain functional groups capable of forming hydrogen bonds and in which the hindrance effect is not so strong, the probability for the hydrogen bonds to appear is very high; sometimes they have significant energies which require detailed studies [1–4].

Most papers which study the hydrogen bond in polymers use experimental results obtained through IR absorption spectrometry. The importance of this method is due to the vibrational mode sensitivity to the intermolecular interactions; because of the association the vibrational modes are disturbed and the absorption maxima shift towards low frequencies and the absorption band intensities modified.

The present paper studies the hydrogen bonds in styrene-(mono-ethyl-maleate) copolymer (ST-MEM), pointing out the experimental determination of the number of intermolecular interactions and of the value of hydrogen bond energy.

2. Experimental procedure

The synthesis of ST-MEM copolymer was carried out by styrene copolymerization with maleic anhydride at 70 °C, in ethanol as the reaction medium [5]. The copolymer was purified by dissolution and precipitation, and analyzed by IR-spectrometry. The thin and homogeneous films prepared for the IR analysis measurement were cast from 3% (w/v) ethanol solutions onto NaCl windows, at room temperature. After the evaporation of the most part of the solvent, the films were transferred to a vacuum dessicator to remove the residual solvent and then stored under vacuum.

For these films, infrared spectra were obtained on a Specord M-80 IR-spectrometer. The spectra recorded at elevated temperatures were obtained by using a heating cell mounted inside the sample compartment of the spectrometer. Temperature control was performed by a heat controller to a reported accuracy of ±0.5 °C. Films used in this study were sufficiently thin to be within the absorbance range where the Beer-Lambert law is applied.

In IR spectra of ST-MEM copolymer we notice the presence of the absorption bands corresponding to the polyesters and monosubstituted aromatic rings. In the stretching vibrations regions of –C=O groups, absorption bands generated by the stretching vibration of the esteric (1738 cm^{-1}) and carboxylic (1712 cm^{-1}) groups, respectively, appear (Fig. 1).

The shift of hydroxyl groups vibrational frequency towards low frequency and the presence of carbonyl group absorption band at 1712 cm^{-1} show an association of acid type hydrogen bonds. Consequently, the hydroxyl group absorption band is broad, without a determined structure and situated at about 3000 cm^{-1} being partially covered by the ν(CH) vibration of aromatic ring (3100–3000 cm^{-1}) and ν_s and ν_{as} stretching vibrations of CH_2 and CH_3 groups (between 3000 and 2800 cm^{-1}).

The styrene content in the copolymer (∼24% w/w) was determined by using the analytical band with the absorption maximum at 1592 cm^{-1} corresponding to ν(C-C) vibration of monosubstituted aromatic ring and whose frequency and intensity is insensitive to the alkyl radical nature [6]. For the calibration curve we used poly(styrene) synthetized in our laboratory.

To avoid performing the measurements of the polymer film thickness (it is not convenient for our particular purpose because it requires very thin films), the internal sample thickness method was applied using

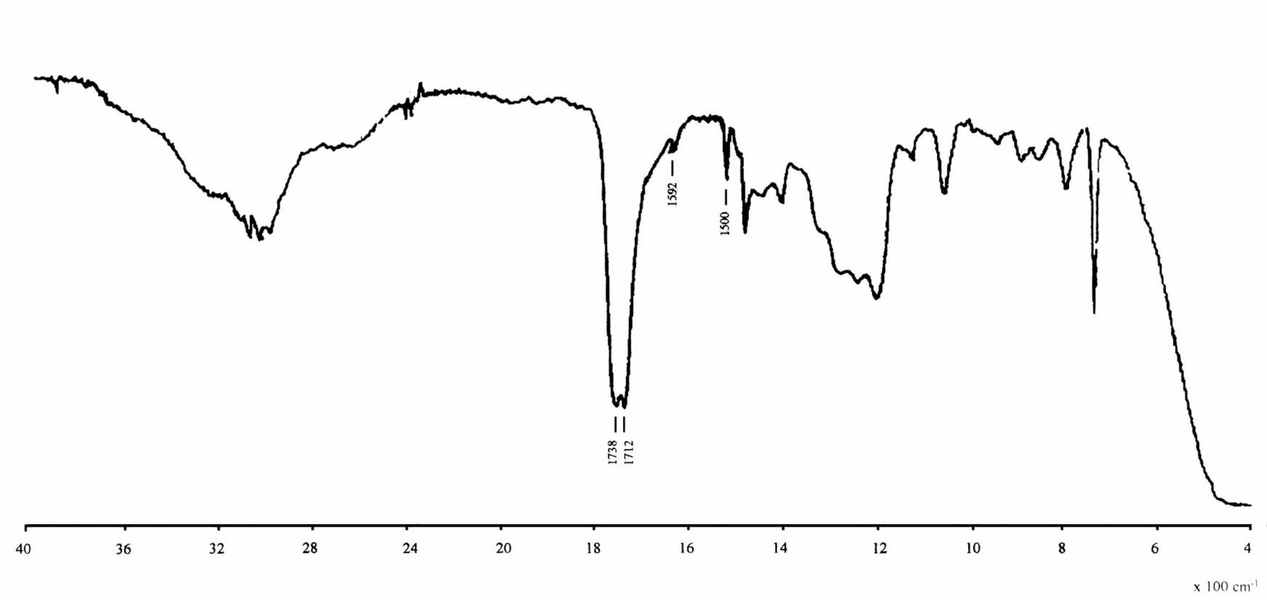

Figure 1 IR spectra of ST-MEM recorded in the 4000–400 cm^{-1} region, at room temperature.

the absorbance of some other band in the spectrum. The 1500 cm^{-1} styrene ring mode appears unaffected by the presence of polyesters and may be considered an internal standard.

3. Results and discussions

We subtracted the absorption band from 1738 cm^{-1} by introducing an identical amount of saturated ester in the IR beam. Elevated temperature registering (above 90 °C) reveal an absorption band attributed to the "free" (unbonded) carboxylic groups at 1758 cm^{-1} and the decreasing of the absorption band intensity of the bonded carboxylic groups at 1712 cm^{-1}. To avoid thermo-oxidative degradation the maximum temperature was 140 °C. Returning to room temperature the absorption band of "free" carboxylic groups disappears and the absorption band from 1712 cm^{-1} returns to the initial absorbance (Fig. 2). This can be explained by the hydrogen bond breaking under the heat action. When the heat action stops the hydrogen bond recovers, the process being reversible.

The associated group fraction was determined using the following relation:

$$f^a = \frac{A^{1712}}{A^{1712} + a_r A^{1758}} \qquad (1)$$

where A^{1712} and A^{1758} represent the absorption band areas at 1712 and 1758 cm^{-1} and a_r is a correlation factor used because of the different absorptivities of the two absorption bands. We used an absorptivity ratio of 1.5 [7–9].

TABLE I Fraction of H-bonded carboxylic acid groups at different temperatures

	Carboxylic acid dimer C=O band		"Free" C=O band		
t (°C)	ν (cm^{-1})	Area	ν (cm^{-1})	Area	f^a (%)
130	1712	1483	1758	224	81.5
120	1712	1514	1758	191	84.1
110	1712	1548	1758	153	87.1
100	1712	1560	1758	138	88.3
90	1712	1632	1758	128	89.5

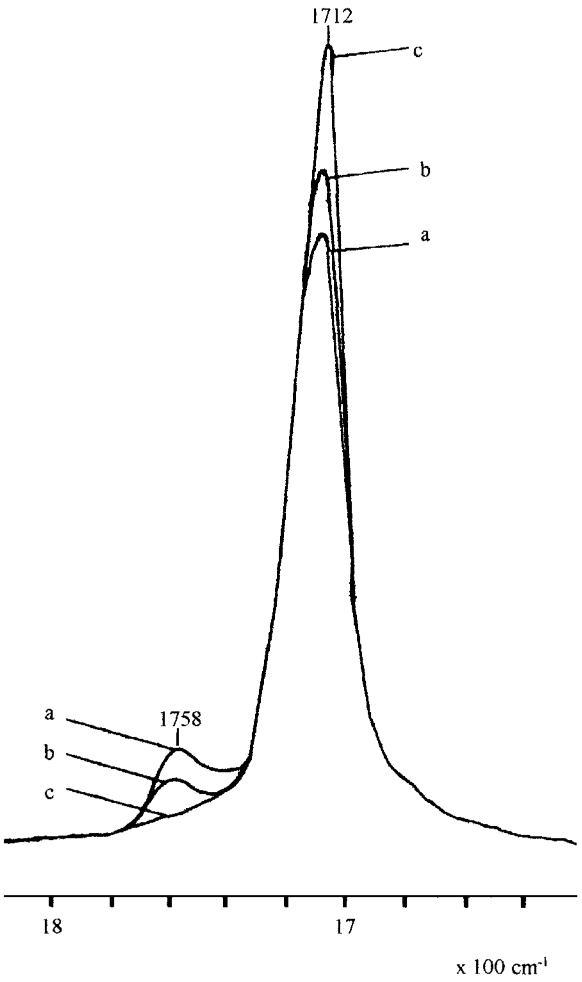

Figure 2 Scale expanded infrared spectra in the carbonyl stretching region of ST-MEM recorded as a function of decreasing temperature: (a) 130 °C; (b) 100 °C; (c) cooled at room temperature.

Table I lists the absorption band areas and the bonded carboxylic acid group fraction at different temperatures.

Using the data presented for the experimental fraction, the nondimensional equilibrium constants (K_a) which describe the dimer formation are obtained using an expression in which the equilibrium constants are related to the fraction of associated molecules (f^a):

$$K_a = \frac{f^a(2 - f^a)}{4(1 - f^a)^2} \tag{2}$$

The experimental values obtained are given in Table II.

Having obtained equilibrium constants at five different temperature we may calculate the enthalpy and entropy of hydrogen-bonded dimer formation from the slope and intercept of the van't Hoff plot (Fig. 3) yielding values of: -4.2 kcal mol^{-1} and -3.7 e.u. mol^{-1}.

TABLE II Self-association equilibrium constants for H-bonded carboxylic acid groups at different temperatures

t (°C)	90	100	110	120	130
K_a (nondim)	22.4	18.0	14.1	9.6	7.1

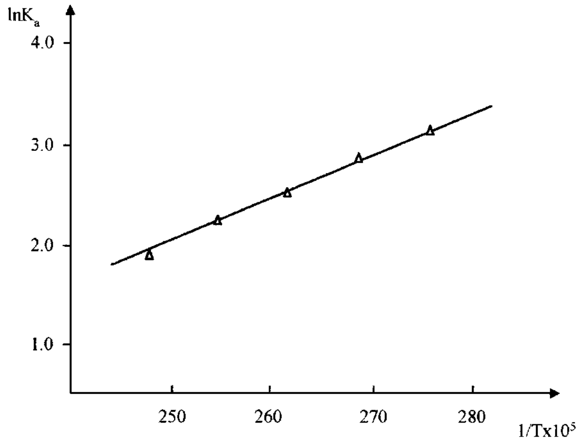

Figure 3 Graph of $\ln K_a$ versus T^{-1}.

4. Conclusions

Thin and homogeneous films of styrene-(mono-ethyl-maleate) copolymer were studied by using infrared spectrometry. The absorbance at 1712 and 1758 cm^{-1} assigned to the dimer and monomer carboxyl stretching, respectively, can be used in infrared analysis to determine the temperature dependence of hydrogen bonding. From the energetic consideration of hydrogen bond the enthalpy was estimated to be -4.2 kcal mol^{-1}. This value is relatively small compared with these of the ordinary stable hydrogen bonding. However, hydrogen bonds in this type of copolymer are very important in considering the properties and it may lead to a wide range of applications.

References

1. G. MOISE, I. HOGEA and C. ANDREI, *Mater. Plast.* **33**(4) (1996) 240.
2. G. MOISE and C. ANDREI, *ibid.* **33**(3/4) (1997) 193.
3. C. ANDREI and G. MOISE, *Rev. Chim.* **48**(10/11) (1997) 851.
4. *Idem.* "Symp., III-ème Seminaire Franco-Roumaine Sur Les Polymers," Neptun, Romania, 1997.
5. C. ANDREI, *Mater. Plast.* **11**(1) (1974) 18.
6. M. AVRAM and G. D. MATEESCU, "Infrared Spectrometry" (Editura Tehnica, Bucharest, 1966) p. 278.
7. E. J. MOSKALA, S. E. HORVE, P. C. PAINTER and M. M. COLEMAN, *Macromolecules* **17** (1984) 1671.
8. M. M. COLEMAN, C. J. SERMAN and P. C. PAINTER, *ibid.* **20** (1987) 226.
9. J. Y. LEE, P. C. PAINTER and M. M. COLEMAN, *ibid.* **21** (1988) 346.

Received 31 July
and accepted 14 October 1998