Thermoplastic Elastomers by Hydrogen Bonding
2. IR-Spectroscopic Characterization of the Hydrogen Bonding

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SUMMARY

By reacting polybutadiene with 4-Phenyl-1,2,4-triazoline-3,5-dione (PTD) urazole groups are added to the polymer. The formation of hydrogen bonds between different urazole groups is investigated by IR-spectroscopy at various temperatures. The carbonyl stretching vibrations at 1700 and 1723 cm^{-1} could be attributed to hydrogen bonded and free urazole groups. With increasing temperature the fraction of bonded groups decreases. From the overall change in the absorption the ratio of the extinction coefficients of bonded and free C=O is determined. The stability of the hydrogen bonds is explained by a chelate like complex between two urazole groups.

INTRODUCTION

The reaction of 4-substituted 1,2,4-triazoline-3,5-diones with polydienes gives rise to a strong change in the polymer properties (1,2). This change in properties has been attributed to the formation of hydrogen bonds between two urazole groups as shown schematically in figure 1.

In a previous study (3) the first results dealing with the rheological characterization of modified polybutadiene have been reported. It was found that the rubber plateau is broadened corresponding to an apparent increase of the molecular weight. From the analysis of the temperature dependence of the viscoelastic response it turns out that the change in the activation energy of local flow processes is a function of the effective number of hydrogen bonds (3,4).

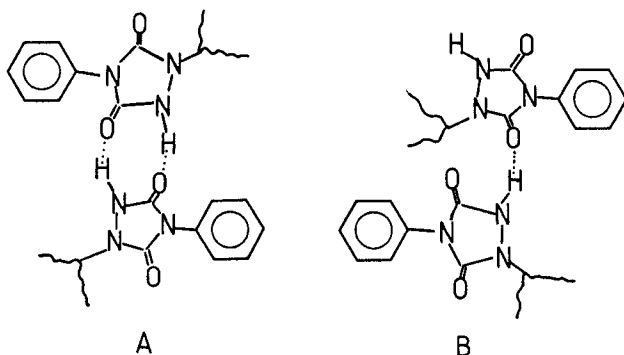* To whom offprint requests should be sent

figure 1: Schematical representation of the basic types of hydrogen bond complexes between two urazole groups; A = chelate - like complex with 2 hydrogen bonds; B complex with 1 hydrogen bond

In the present communication we report on infrared spectroscopy experiments to characterize spectroscopically the hydrogen bond interaction. Temperature dependent measurements have been performed in the temperature range between 40 and 80°C. The polymer used in this study is a narrow distributed polybutadiene (Mn=48500, Mw/Mn=1.05) which has been modified using 1 mol-% of 4-Phenyl-1,2,4-triazoline-3,5-dione. A detailed description of the modification procedure is given in the previous paper (3). The polymer used in the present study has been designated as PB50-1.

RESULTS AND DISCUSSION

The two carbonyl functions of the urazole groups give rise to strong absorptions at 1770 and 1700 cm^{-1} (1). It has been shown by BUTLER that for some cases in the NH-stretching region at 3100 - 3500 cm^{-1} two bands can be detected in modified polymers which have been attributed to bonded and unbonded hydrogen atoms. There has been no indication that a distinction between hydrogen bonded and free urazole groups can be made from the C=O stretching vibration.

In figure 2 the infrared spectra of the carbonyl stretching region between 1600 and 1800 cm^{-1} are shown for various temperatures. It is evident that the absorption line at 1700 cm^{-1} shows a shoulder at higher frequency (1723 cm^{-1}). With increasing temperature the intensity of the 1701 band decreases while the intensity at 1723 cm^{-1} increases. The second C=O stretching vibration at 1770 cm^{-1} remains unchanged with temperature variation.

WAVENUMBER (cm^{-1})

1800   1750   1700   1650   1600
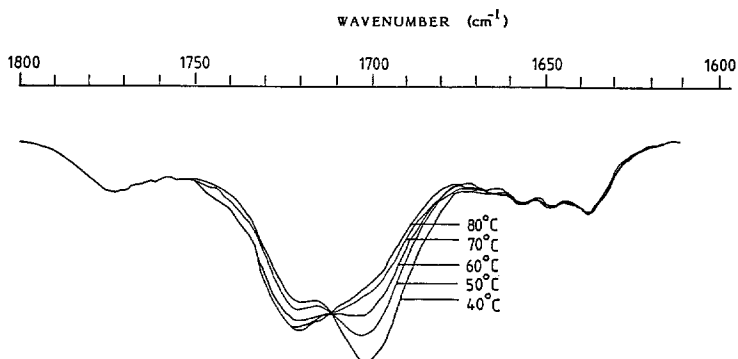
80°C
70°C
60°C
50°C
40°C

Figure 2: Temperature dependent infrared spectra of the C=O -
stretching region of 1% modified polybutadiene (PB50-1); tem-
peratures as indicated;

As is known from other types of hydrogen bond forming functio-
nal groups like in polyamides or polyurethanes, the hydrogen
bonded carbonyl stretching vibration is shifted to lower fre-
quency compared to the vibration of the   free   group.   The
shift is in the order of 20 wave numbers.   The experimental
result observed for the urazole groups in the modified poly-
butadiene is equivalent.
The absorption at 1723 cm^{-1} has to be attributed to   free
carbonyl while the absorption at 1701 cm^{-1} corresponds to the
carbonyl stretching vibration of groups involved in hydrogen
bonds.
An important feature is that the band at 1770   cm^{-1} being
attributed to the second C=O stretching vibration (1) does not
change with temperature. This indicates that the two carbonyl
groups in the urazole are not equivalent with respect to the
formation of hydrogen bonds.   In figure 1 the possible
structures of complexes formed by two urazole groups are
shown. It is evident that the stability of structure A where
two hydrogen bonds are formed per complex is enhanced compared
to structure B where only one hydrogen bond is formed.   Due to
the high flexibility of the elastomeric matrix and the fact
that by rotation around one bond the urazole groups may be
rearranged to form the favoured complex A this structure will
be dominant. Thus the bands at 1700 (1723) cm^{-1} and 1770 cm^{-1}
may be assigned to the different C=O groups of the urazole
ring.

With increasing temperature the fraction of free carbonyl in-
creases. The analysis of the C=O as well as N-H stretching
vibration has been used quite often to estimate thermodynamic
parameters associated with hydrogen bond formation (5).   In
recent work it has been pointed out that the analysis normally
used may bear some serious errors (6).   The thermodynamic

analysis requires the knowledge of the mole-fraction of bonded and unbonded groups as a function of temperature. To get these data from the infrared spectra the absorption coefficients or at least the ratio of the absorption coefficients of the corresponding bands must be known. In addition the analysis only will be successful if the position of the bands do not change with temperature, i.e. if the average stability of a hydrogen bonds remains unaltered. This is not the case for a system like amorphous polyamide (6). The occurence of a isosbectic point (figure 2) shows that in the present system the bands do not shift seriously with temperature i.e. there are only two absorbing species in the system. This may be a consequence of the chelate like type of hydrogen bond interaction (fig1 A). The occurence of the isosbectic point prooves that the extinction coefficients do not change with temperature (all spectra were run under identical conditions on the same sample).

The spectra could be fitted with two lorentzian lines. The experimental spectra and the best fits are given in figure 3. To get the best fits the position at 1723 cm^{-1} had not to be changed; the band of bonded C=O at 1701 cm^{-1} had to be shifted for one wavenumber for the highest temperatures. The half width of the 1701 cm^{-1} band had to be changed with raising temperature from 14 to 16 cm^{-1} respectively. The data are given in table 1 as well as the relative areas and the total change in area. The lowest temperature has been taken as reference (40°C = 100).
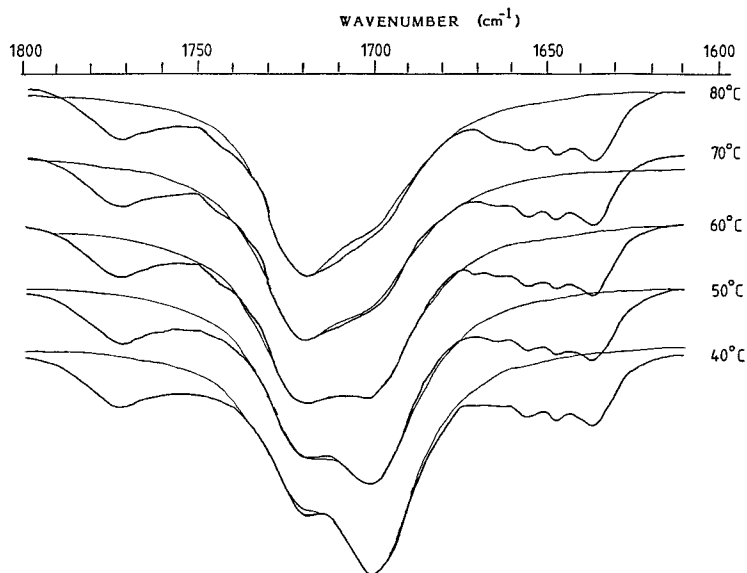

Figure 3: Experimental spectra of the C=O stretching vibration and best fit using two lorentzian lines for various temperatures. Fit parameters are given in table 1

Table 1: Analysis of the C=O stretching vibration of PB50-1
   data were obtained by curve fitting using two lorentzian
         lines

T	free C=O			bonded C=O			
	wave- number	half- width	rel. int.	wave- number	half- width	rel. int.	total area
°C	cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}		
40	1723	13	.31	1701	14	.69	100
50	1723	13	.4	1701	14	.6	97
60	1723	13	.49	1701	15	.51	90
70	1723	13	.54	1702	16	.46	88
80	1723	13	.58	1702	16	.42	85

The total area decreases with temperature. This change in the
overall area can be used to calculate the ratio of the extinc-
tion coefficients $f = \varepsilon\,1701/\varepsilon\,1723$ (7) if the extinction
coefficients do not change strongly with temperature which is
shown by the existence of a isosbectic point.

The total absorption of the carbonyl region (only the 1723 and
1701 bands are considered) is given by

$$A^t = \varepsilon_1 c_1 + \varepsilon_2 c_2$$

The index 1 denotes the free, index 2 the bonded carbonyls.
ε_i is the respective absorption coefficient, c_i the concentra-
tion. If the   formation of the hydrogen bonds between   two
urazole groups U can be described by a simple equilibrium
according to

$$2\,U \xrightarrow{\ K\ } U_2$$
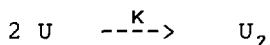
c_1 and c_2 are the concentrations of free and bonded urazole
groups, and may be expressed by the mole fractions x_i and the
total concentration c_0 of urazole groups $(c_i = x_i * c_0)$. If f
is the ratio of the extinction coefficients $\varepsilon\,1701/\varepsilon\,1723$ the
total reduced absorption may be written as

$$A^t_{red} = A^t/c_0 = x_1\varepsilon_1 + f * \varepsilon_1(1 - x_1)$$

f may be obtained if the relative changes in the area of the bands corresponding to the free and bonded urazoles of two temperatures are compared. A knowledge of the mole fractions is not required.

$$1/f = - \Delta A_1 / \Delta A_2$$

where ΔA_i is the change in area of the band i if the temperature is raised for ΔT.

In figure 4 the increase of the free carbonyl is plotted versus the decrease of the bonded carbonyl intensity. From the slope the ratio of the extinction coefficients $f = 2.1$ is obtained. Values reported in the literature for polyamides and polyurethanes are in the same order (8).
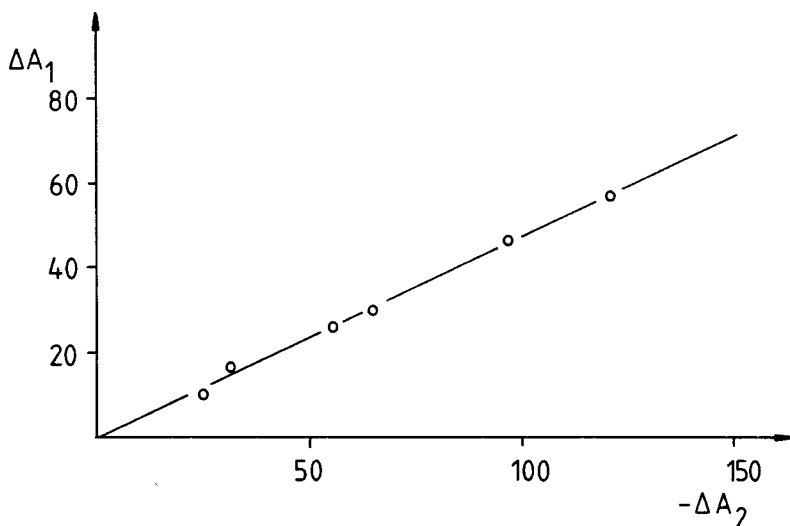

Figure 4: Plot of the increase of the band corresponding to the free carbonyl groups versus the decrease of the intensity of the band corresponding to the bonded groups. From the slope f is obtained.

With the knowledge of f the mole fractions of bonded and free urazole groups (x_1 and x_2) can be calculated as well as the equilibrium constant for the formation of hydrogen bonds. The data are collected in table 2.

Table 2: Calculated mole fractions of free and bonded urazole groups and the equilibrium constant K for the formation of hydrogen bonds as a function of temperature

T °C	x_1	x_2	K 1/mol	ln K
40	0.485	0.515	109	4.7
50	0.585	0.415	60	4.1
60	0.666	0.334	37	3.6
70	0.71	0.29	28	3.3
80	0.74	0.26	23	3.1

A more detailed analysis including a discussion of the N-H vibration and a comparison with data obtained from mechanical measurements will be given elsewhere (4). A thermodynamic analysis of the equilibrium constants in terms of the van t' Hoff equation may be performed but the values for the enthalpy of formation of the hydrogen bonds will be quite erroneous due to the relatively small temperature range under investigation.

It should be pointed out that the analysis as described is possible because the shift of the 1701 cm^{-1} band as well as changes of the absorption coefficients with temperature are negligble. This may be a consequence of the type of hydrogen bond. The shift in the band position in other systems has been attributed to an increase in the average length of the C=O...H-N distance (weakening of the bond). In the case of a chelate like complex A two hydrogen bonds are formed per complex and a shift of the band is not observed.

ACKNOWLEDGEMENT

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