Monitoring of Curing of Polyurethane Polymers with Fluorescence Method

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ABSTRACT: In the present study a fluorescence technique and nine fluorescence probes have been applied to monitor the curing of polyurethanes. As the curing proceeds, the fluorescence emission bands of the probes exhibit hypsochromic shifts due to the increase in the environmental microviscosity. An intensity ratio method was developed, where ratios of the low- to high-intensity changes (LHIC) in the emission bands were used to determine the degree of the curing process. The method enables one to follow the changes in the polymer structure throughout the entire curing process and to obtain comparable results from different types of probes during the same curing process and is independent of the probes or the polymers. The technique can be applied to a variety of commercial and industrial polymers.

Introduction

Several methods such as differential scanning calorimetry[1] (DSC), photodifferential scanning calorimetry[2] (PDSC), laser interferometry,[3] photoacoustic spectroscopy,[4] and FTIR spectroscopy[5] have been developed to follow polymerization. However, DSC methods are not suitable for monitoring real-time processes or for the nondestructive analysis of polymers. FTIR is widely used to determine the degree of polymerization by monitoring the concentration of residual monomers present in polymer systems. A real-time infrared technique was developed by Decker et al.,[6] but the technique can only be used for analyzing thin films and cannot be used for coatings or bulk materials.

Fluorescence spectroscopy has gained considerable interest as a tool for monitoring the curing of polymers because of its high sensitivity, selectivity, and nondestructive characteristics.[7] Fluorescence probes are widely used in chemistry for monitoring specific properties of the medium in which they are incorporated. An important application of fluorescence probes in polymer chemistry is the monitoring of a polymerization process. Loutfy[8] first studied polymerization processes using the fluorescence of a series of donor−acceptor probes. It was proposed that an enhancement in the microviscosity of the medium leads to a decrease in the nonradiative decay rate and consequently an increase in the fluorescence quantum yield. Torkelson[9] investigated molecular relaxation using fluorescence probes. During the process, a significant increase in the medium viscosity was observed. Therefore, probes whose emission is sensitive to the rigidity of their environment are specifically suitable for this purpose. Probes whose intensity increases upon the polymerization[8] or during other rigidification processes such as physical aging[9] and probes whose emission wavelengths shift during polymerization process[10] are well-known.

Fluorescent probes are widely used for monitoring the curing process, e.g., excited dimer forming molecules[11] such as pyrene or its derivatives, intramolecular charge-transfer molecules[12] such as 6-propionyl-2-(dimethylamino)naphthalene (PRODAN), and organic donor−acceptor salts[13,14] such as 2(4-(4-(dimethylamino)phenyl)-1,3-butadienyl)-3-ethylbentzothiatzole *p*-toluenesulfonate (STYRYL7). Recently Neckers et al.[15,16] reported the use of fluorescence probes for monitoring the curing process of polyolacrylate monomers with an intensity ratio method.

The use of nonreactive fluorescence probes that exhibit intramolecular charge-transfer properties and stereoisomerism have been reported.[8] In the present study seven intramolecular charge-transfer probes were selected. The probes contain both an electron donor and an electron acceptor being linked by an aromatic chromophore. Because both twisting and charge separation are involved in the formation of intermolecular charge transfer states, the fluorescence emissions of the probes are sensitive to both solvent polarity and medium microviscosity. Blue shifts of the emission spectra of the probes can be observed due to the increase in medium viscosity. This makes it more difficult to form long wavelength twisted conformations in excited states for internal charge-transfer probes.[17,18]

Organic donor−acceptor probes such as D-π-A,[19] D-σ-A,[20] and D-π-A^+X^- [21] have been reported. We chose two organic salts (D-π-A^+X^-) containing an organic cation, an alkylated pyridinium ion linked to an aromatic dimethylamine by a π-system, and an inorganic or organic anion. These salts are specifically sensitive to the rigidity of their environment but nonsensitive to the temperature and the solvent polarity. The ability of these probes to monitor the rigidity of their environment is explained by the decreased mobility of the counterion. Since the anion is less mobile in a polymer environment, a blue shift upon the polymerization is expected. The lack of solvatochromism can be explained by electrical properties, the ground state and the lowest excited state are roughly equivalent.[21]

In this paper, we present the results of our recent study that used different types of probes and improvement of the intensity ratio method for finding comparable results from different types of probes and polymers. Our results indicate that the technique is both versatile and of general applicability in a variety of curing systems; it is independent of both probes and polymers. Remote sensing can be achieved by using fiber-optic cables to transmit optical signals to and from a polymerization system in real-time.

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Table 1. Configurations of Polyurethanes

name	first comp, polyol	second comp, isocyanate	accelerator
PU1096	polyether/polyester (58.7 wt %)	hexamethylene diisocyanate (41.3 wt %)	dibutyltin dilaurate (0.117 wt % on polyol)
PU1391	hexanedyol (28%)	hexamethylene diisocyanate (72 wt %)	dibutyltin dilaurate (0.05 wt % on polyol)
PU1426	polypropylene glycol (41.7 wt %)	polyisocyanate (58.3 wt %)	dibutyltin dilaurate (0.02 wt % on polyol)

Table 2. Absorption and Emission Maxima of the Probes in Selected Solvents

probe	λ_{max} abs (nm)	λ_{max} em (nm)	probe	λ_{max} abs (nm)	λ_{max} em (nm)
4HP[a]	469	572	DAM[b]	333	527
CO152[a]	394	474	DASQI[b]	523	620
DANBP[a]	407	675	LAURDAN[b]	360	494
STYRYL7[a]	599	699	PRODAN[b]	361	495
DAZ[b]	343	552			

[a] $CHCl_3$. [b] MeOH.

Experimental Section

The components of three types of polyurethanes, type codes PU1096, PU1391, and PU1426, were obtained from GAIRESA Co., Spain. The component configurations are shown in Table 1. The polyurethane polymers that were studied had an intrinsic fluorescence emission, but the emission was not suitable for studying the curing process. Thus, after a selection process, nine probes were chosen and tested for their suitability for monitoring the curing process of the polyurethane polymers. The structures of the chosen probes and the abbreviations used in this paper are shown in Figure 1.

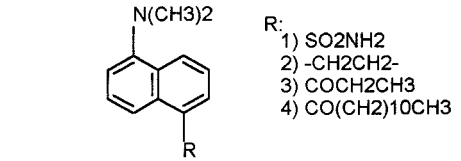
7-(Dimethylamino)-4-(trifluoromethyl)coumarin [CO152], *N*-(5-(dimethylamino)naphthalene-1-sulfonyl)aziridine [DAZ], 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran [4HP], and, 2-(4-(dimethylamino)styryl)-1-methylquinoliniumiodide [DASQI] were purchased from Aldrich. 1,6-Propionyl-2-(dimethylamino)naphthalene [PRODAN], 10,6-dodecanoyl-2-(dimethylamino)naphthalene [LAURDAN], and 5-(dimethylamino)naphthalene-1-sulfonamide [DAM] were purchased from Molecular Probes. 4-(Dimethylamino)-4'-nitrobiphenyl [DANBP] and 2(4-(4-(dimethylamino)phenyl)-1,3-butadienyl)-3-ethylbentzothiatzole *p*-toluenesulfonate [STYRYL7] were purchased from TCI and Kodak, respectively. All the probes were spectroscopic grade and used as received without further purification.

The polymer samples were prepared, and the curing was monitored as follows. The fluorescence probes were doped (0.25×10^{-3} mol dm^{-3}) into the polyol, the first component, and then mixed with the second component. Mixtures were made for polyurethanes PU1096, PU1391, and PU1426 in weight ratios of 1.42:1.0, 0.38:1.0, and 1.40:1.0, respectively. The mixtures were sandwiched (0.05 mg) between two glass plates, and the thickness of the mixtures was controlled by a double-coated tape (92 μm). Curing processes were monitored at 21 °C.

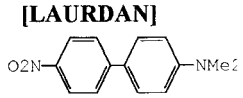
Fluorescence was recorded using a Spex Fluorolog 3 spectrofluorometer in the front-phase mode for polymeric films and at right angles for the solutions. Remote measurements were carried out using a fiber-optic cable attached to the excitation and emission monochromators. Absorption spectra were recorded on a Shimadzu UV-2501PC, UV−vis recording spectrophotometer. Infrared measurements for determining the curing conversion were performed using a Perkin-Elmer FTIR spectrometer 1725X with a spectral resolution of 4 cm^{-1}. The extent of curing could be monitored from a decrease in the isocyanate band at 2271 cm^{-1}, and the conversion was calculated using the following equation:

$$\alpha = 1 - \frac{A_{iso}(t)\, A_s(0)}{A_{iso}(0)\, A_s(t)}$$

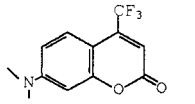
where $A_{iso}(t)$ and $A_{iso}(0)$ are the absorbances at 2271 cm^{-1} at the curing times of t and 0. $A_s(t)$ and $A_s(0)$ are the absorbances of the CH band at 2960 cm^{-1} at the corresponding times which used an internal standard peak to compensate the changes of the thickness and the opacity in the samples during the curing process.[5]



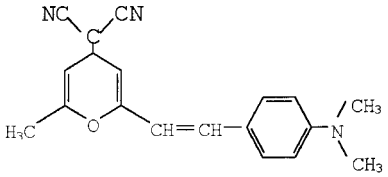
1) 5-[dimethylamino] naphthalene-1-sulfonamide, **[DAM]**
2) N-(5-dimethylamino naphthalene-1-sulfonyl) aziridine **[DAZ]**
3) (1,6-propionyl-2-dimethylamino naphthalene) **[PRODAN]**
4) (10,6-dodecanoyl-2-dimethylamino naphthalene) **[LAURDAN]**



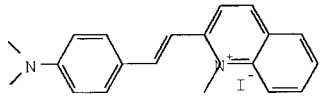
4-dimethylamino-4´-nitrobiphenyl **[DANBP]**



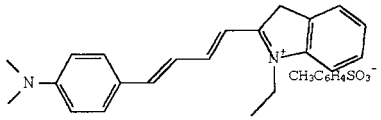
(7-(dimethylamino)-4-(trifluoromethyl) coumarin) **[CO152]**



4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran **[4HP]**



2-(4-(dimethylamino)styryl)-1-methylquinolinium iodide, **[DASQI]**



(2(4-(4-(dimethylamino-)phenyl)1,3-butadienyl)-3-ethylbentzothiatzole p-toluene sulfonate), **[STYRYL7]**

Figure 1. Chemical structures and abbreviations of nine probes which were used for monitoring the curing process of polyurethanes PU1096, PU1391, and PU1426 by fluorescence spectroscopy.

Results and Discussion

Aromatic amines possessing strong donor and acceptor substituents often exhibit intramolecular charge-transfer properties with large Stokes shifts or dual fluorescence. For monitoring the curing of polymers, a high fluorescence quantum yield and a large Stokes shift are advantageous for the probe. Blue shifts in fluores-

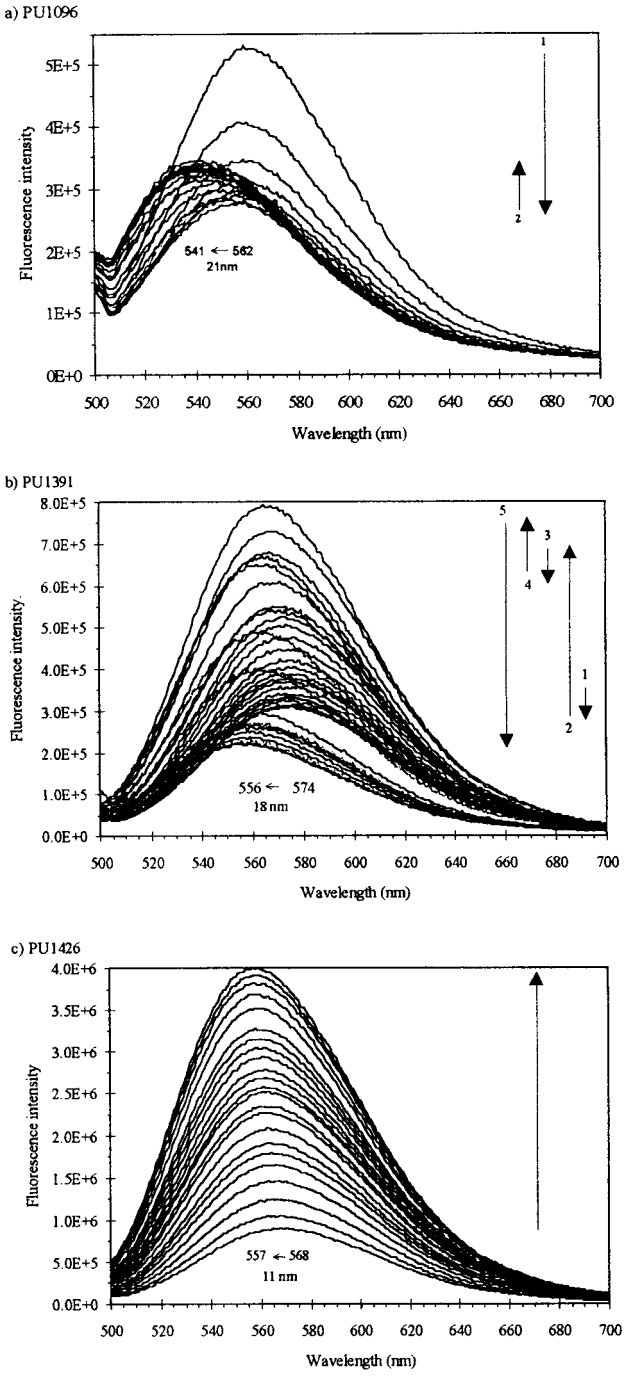


Figure 2. Fluorescence emission spectra of 4HP probe during the curing process of polyurethanes at room temperature. The arrows show the order of spectra during the curing processes.

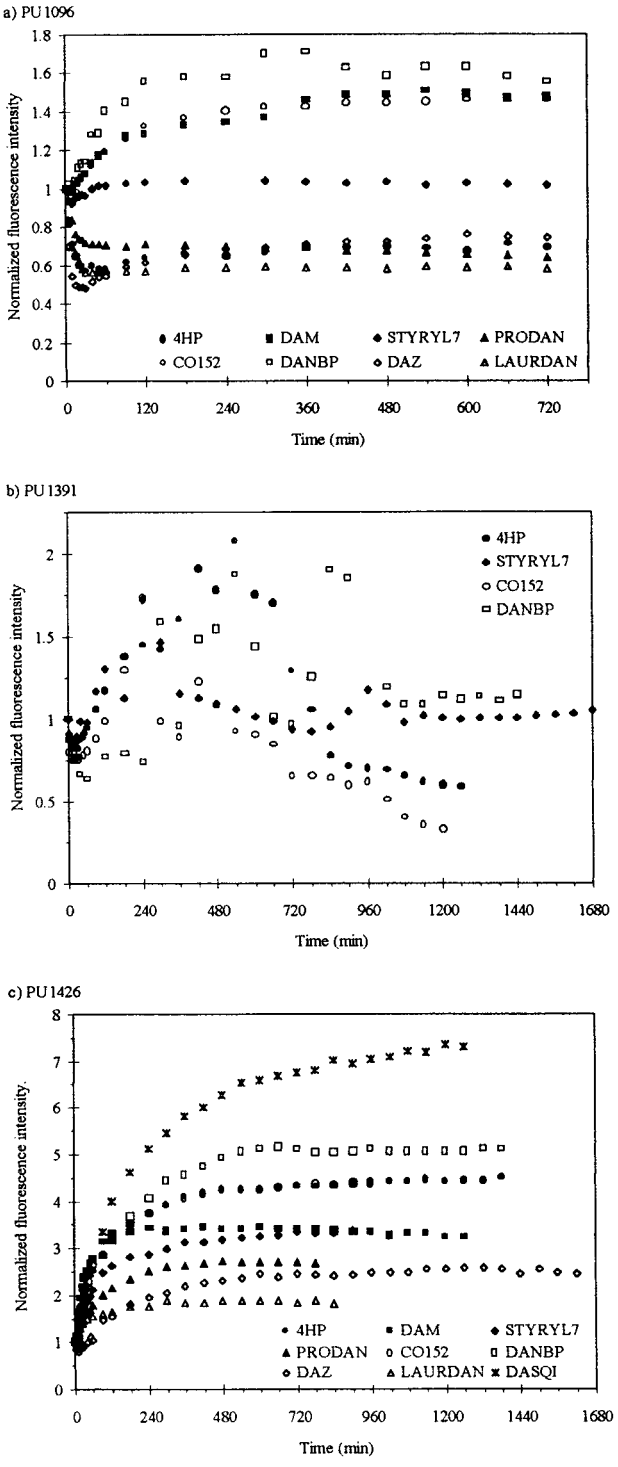


Figure 3. Normalized fluorescence intensities of the emission maxima as a function of the curing time at room temperature for eight probes in PU1096, four probes in PU1391, and nine probes in PU1426.

cence emission indicate increasing viscosity during the curing process. The large difference between the absorption and emission bands offers a wider spectrum window. The possible intrinsic fluorescence of the polymer would interfere less with the fluorescence signal of the probe. Absorption and emission maxima of the selected probes in some solvents are summarized in Table 2.

The curing of the polyurethanes was monitored by measuring the broad fluorescence emission bands of the probes as a function of the curing time at a constant temperature, 21 °C. The probes emitted at different wavelengths behaved differently depending on the probe and the polyurethane. Eight probes for PU1096, four probes for 1391, and nine probes for PU1426 exhibited behavior that made it possible to use them for monitoring the curing process. The changes in the wavelengths for each successful probe in polyurethanes are presented in Table 3. An overlap of the emission bands of the probe and the polyurethane and a weak emission intensity or quantum yields were the main reasons for rejecting some of the probe−polymer systems.

The probes that could be used for monitoring the curing processes exhibit significant blue shifts upon polymerization. The largest spectral shifts were observed for DANBP. The blue shifts are effected by the type of polyurethane used. It is evident that the

Table 3. Wavelength Changes of the Emission Maxima during the Curing Process at Room Temperature and the Wavelengths That Were Chosen for Calculation of the Fluorescence LHIC Ratio for the Polyurethanes

	polyurethane					
	wavelength changes of the emission maxima during the curing process (nm)			wavelengths chosen for the fluorescence LHIC ratio (nm)		
probe	PU1096	PU1391	PU1426	PU1096	PU1391	PU1426
4HP	22 (562→541)	18 (574→556)	11 (568→557)	600/510	660/515	650/510
CO152	16 (476→451)	17 (476→456)	9 (473→464)	555/420	520/440	580/425
DASQI			8 (592←584)			690/580
STYRYL7	12 (672→660)	26 (684→658)	5 (674→669)	700/610	715/635	700/625
DANBP	33 (552→519)	30 (570→540)	17 (566→549)	640/495	650/510	650/500
DAZ	27 (494→467)		12 (504→492)	550/450		590/465
DAM	19 (466→447)		9 (478→469)	540/435		590/445
PRODAN	10 (430→420)		7 (429→422)	480/390		490/405
LAURDAN	10 (428→418)		5 (430→425)	445/410		510/405

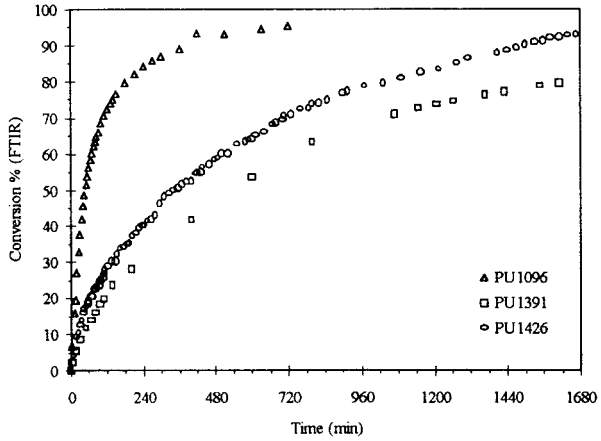


Figure 4. Conversion percentages of the polyurethanes at room temperature determined by FTIR as a function of the curing time.

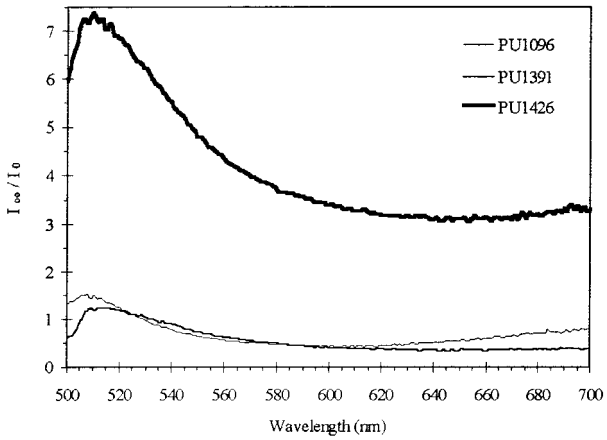


Figure 5. Ratio of the fluorescence intensities (I_∞/I_0) of 4HP probe in the curing process of the polyurethanes at room temperature as a function of wavelength.

magnitude of the shift increases with a decrease in the polarity of the environment. This causes the main differences in the emission band positions. The hypsochromic shifts observed by the studied probe−polymer systems, however, could not be used alone as reliable indicator for the curing degree. Only one probe, STYRYL7, of the two probes from the organic D-π-A^+X^- salts exhibits a reasonable emission band to be used for following the curing process of all polyurethane polymers. The most probable reason is the longer distance of the π-system separates the cation and the dimethylamine groups and the organic structure of the anion. DASQI was useful only for PU1426 and was the only probe that showed a bathochromic shift. DASQI is virtually nonfluorescent in a solvent of low viscosity, such as the monomers, and shows an intense emission only in a polymer environment.

The emission spectra of 4HP during curing of the polyurethanes are shown in Figure 2. As can be seen, the behavior differs, indicating different environmental changes in the polyurethanes. The arrows show the evolution of the spectra during the curing processes. When the cross-linking of a polymer matrix increases, the intramolecular charge transfer or organic salt probes are expected to yield to an increase in fluorescence intensity.[15] Normalized (R/R_0) intensities of the emission maxima of the probes tested are presented as a function of the curing time for the polyurethanes in Figure 3. Some of the probes showed, in the course of the curing, a decrease in the emission intensities in the PU1096 and PU1391 polymers. A decrease in emission intensity with an increase of the viscosity is not a general phenomenon. The conversion percentages of the three polyurthanes determined by FTIR are shown in Figure 4. A comparison of these curves with curves shown in Figure 3 demonstrates that fluorescence intensity changes of the probes are sometimes different in the same environment and cannot always be correlated directly to a conversion percentage.

Thus, to determine the degree of curing, it is necessary to find another method for analyzing the observed data. This method should be independent of the type of polymer or probe and also of the experimental conditions. For this reason we developed a low- to high-intensity change (LHIC) ratio method. In this method the spectrum of the cured polymer, measured at time infinity, was divided by the spectrum of the mixed monomers, measured at time zero. Thus, the intensity changes were obtained as a function of the wavelengths, and the low-intensity changes (LIC) and high-intensity changes (HIC) can be found. The results for the 4HP probe are presented in Figure 5. The wavelengths that were chosen for applying the LHIC ratio method for each probe and polyurethane are listed in Table 3. It can be seen from Figure 5 and Table 3 that the wavelengths that have lowest and highest variation in the intensity changes cover certain wavelength areas. Thus, when the method is applied two wavelengths, areas can be chosen for each probe independent of the polymer.

LHIC curves are obtained by dividing intensities at a certain wavelength in the longer wavelength region to the intensities of certain wavelength at the shorter wavelength region at all moments of the curing time. Normalized LHIC ratios of the selected probes as a function of curing time for the polyurethanes are shown

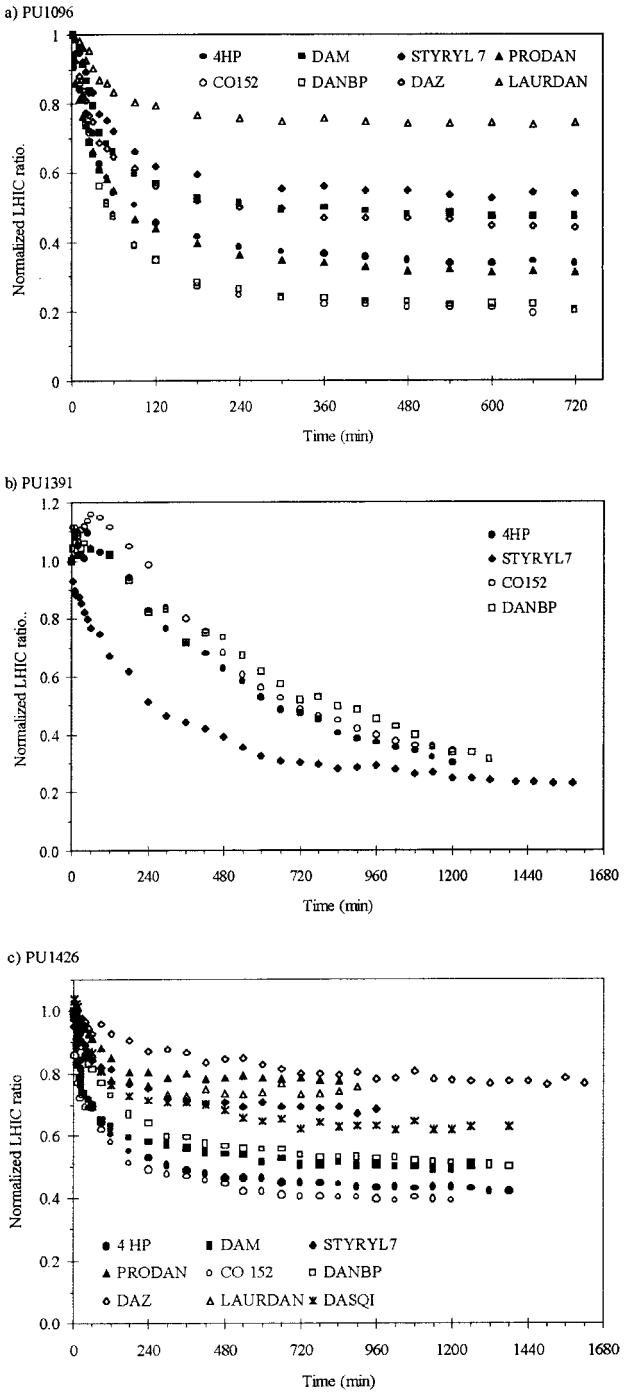


Figure 6. Normalized LHIC ratios of selected probes for the polyurethanes at room temperature as a function of the curing time.

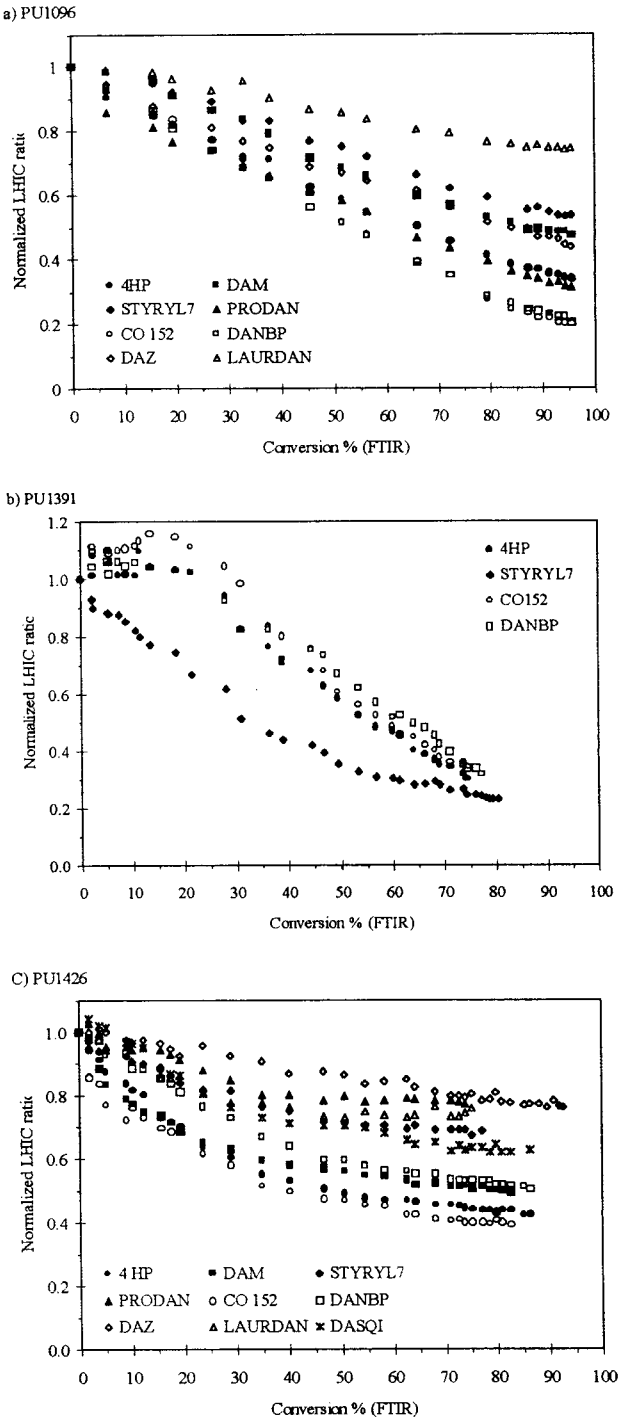


Figure 7. Normalized LHIC ratios of selected probes in the polyurethanes during the curing process at room temperature as a function of conversion measured by FTIR.

in Figure 6. A comparison of these curves with the curves shown in Figure 3 demonstrates that, by applying the LHIC ratio method, similar behavior can be observed for all probes in each polyurethane.

Correlation between normalized LHIC ratios and conversion percentages measured by FTIR are shown in Figure 7 for the polyurethanes. As can be seen, it is possible to obtain similar correlation for all probes in any of the polyurethanes. Linear correlation between LHIC ratio and conversion percentage can be found for the PU1096. The differences in the slopes reflect some useful information such as sensitivity to environment changes. The most sensitive probes are DANBP, 4HP, and CO152 for the PU1096 and the PU1426. It can be seen in Figure 7 that the only probe which is sensitive for the PU1391 during the whole time of the curing process is STYRYL7. The other three probes were insensitive for the polymerization during the first 20% of the curing process by applying the LHIC method. The results show that the LHIC ratio method provides a general method for monitoring the curing of the studied polymers and also a calibration method for avoiding the influence of any artificial changes, e.g., in the sample thickness or lamp intensities during the curing process.

Conclusions

The results show that the fluorescence spectroscopy is a reliable nondestructive measurement system for

monitoring the curing process of polyurethanes. As the curing proceeds, the fluorescence emission spectra of the probes exhibited hypsochromic spectral shifts due to the increase in the matrix microviscosity. A regular correlation between the intensity ratios of fluorescence intensities, selected from the wavelength areas representing the low and highest intensity change (LHIC), and the degree of polymerization were obtained. The advantage of the developed LHIC ratio method is the possibility to follow the composition changes through the curing process independent of the polymer or the probe. The fluorescence cure sensing technique based on the LHIC ratio method can be applied in situ for monitoring the polymerization in a variety of commercial and industrial use of polymers.

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