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Synthesis, characterization and photocross-linking of copolymers of furan and aliphatic hydroxyethylesters prepared by transesterification

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Abstract

Mild experimental conditions were applied to the synthesis of furan-aliphatic photoreactive copolymers by bulk transesterification, which called upon potassium carbonate as the catalyst, reaction times of about 30 h and temperatures ranging from 95 to 120 °C. The ensuing copolymers contained 3–10% of furan photoreactive monomer units, which absorbed at 308 nm, and had molecular weights of about 8000. They were semi-crystalline materials with glass transition temperatures of -51 to -62 °C and were stable up to 225 °C. The irradiation in the near-UV of concentrated solutions or thin films of these copolymers resulted in their cross-linking and suggested their possible use as photoresists, particularly in offset printing plates.

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Keywords: Hydroxyethylesters; Transesterification; Copolymers

1. Introduction

Within the last decade growing attention has been focused on the synthesis of polymers derived from renewable resources (cellulose, lignin, starch, chitin, etc). The interest in this strategy is double: on the one hand, a large variety of products are available either directly or after chemical modification and, on the other hand, these sources are continuously renewed, cheap and ubiquitous.

Our laboratory has been involved for a long time in the valorization of some of these renewable resources [1,2] and among the numerous studies carried out in different domains, special attention has been paid to materials for printing processes, viz. inks [3] and photopolymers for offset plates [4]. In the latter context, the specific properties of the furan heterocycle has been exploited starting from furfural, the most significant industrial chemical of furan-based monomers, obtained by the dehydratation–cyclisation of pentoses contained in the vegetable biomass [5].

Polyesters bearing furan moieties have been the subject of several investigations, beginning with the pioneering studies by Moore's group [6]. Hirai et al. [7] envisaged the use of an A–B type monomer and looked at the possibility of preparing polyesters from 5-hydroxymethyl-2-furoic, but only linear and cyclic oligomers were obtained. Storbekc and Ballauf [8] and Okada et al. [9], studied the polycondensation of furancarboxylic dichlorides with isosorbides and obtained biodegradable materials with good thermal properties. More recently, a series of publications explored the synthesis of a variety of furan polyesters using different procedures and a wide selection of monomers [10]. In particular, Khrouf et al. [11] tackled the use of the transesterification technique and studied the kinetics and mechanisms [12] leading to novel furan polyesters. In all instances [10–12], regular linear macromolecular structures were obtained.

The aim of the present study was to prepare photosensitive polyesters for negative offset plates bearing furan chromophores which can induce their photocross-linking. These chromophores can be introduced in the macromolecular structure either as pendant substituents, as previously

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reported [4], or as an integral part of the main chain, which is the topic of this paper.

2. Experimental

2.1. Materials

Hydroxymethyl furfural (HMF) was synthesized in our laboratory, as described elsewhere [5]. The other reagents, catalysts and solvents were high-purity commercial products used as received.

2.2. Synthesis of 2-hydroxymethyl-5-furanacrylic acid ethyl ester (HMFAE) [13]

10.3 g (8×10^{-2} mol) of HMF, 10.2 g (4.5×10^{-2} mol) of triethylphosphoacetate, 3 g of water and 15 g (2.3×10^{-2} mol) of K_2CO_3 were added to 200 ml of dioxane in a flask equipped with a magnetic stirrer and a reflux condenser. The mixture was heated at 70 °C for 4 h under stirring and then filtered before removing the solvent under reduced pressure. The excess HMF was eliminated by a methylene chloride/-water separation. The organic layer was recovered, dried over Na_2SO_4 and filtered. The solvents were then removed under reduced pressure to give a viscous orange liquid with a yield of 80%.

2.3. Copolymer syntheses

The co-monomers HMFAE and an aliphatic hydroxyethylester, ethyl-6-hydroxyhexonoate (EHH), were mixed with K_2CO_3 in a round-bottomed flask surmounted by a condenser and connected to a vacuum line. The mixture was heated gradually under magnetic stirring and the released ethanol pumped away. At the end of the copolytransesterification reaction, the product was dissolved in THF, precipitated in an excess of cold methanol, filtered and vacuum dried to constant weight at 60 °C.

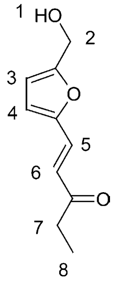
2.4. Film preparation

Methylene chloride copolymer solutions were deposited onto a Teflon plate and allowed to dry. The ensuing polyester films had a thickness of about 50 μm.

2.5. Analytical techniques

^1H NMR spectra were run in CD_2Cl_2 on a Bruker AC200 apparatus. FTIR spectra were recorded with a Perkin–Elmer Paragon 1000 instrument using KBr pellets or NaCl disks. UV–vis spectra were taken with a ThermoSpectronic UNICAMUV 500 equipment using spectrophotometric grade solvents. Differential scanning calorimetry (DSC) was carried out with a Setaram DSC92 calorimeter using aluminium pans. Scans were conducted under nitrogen with a heating rate of 10 °C/min in the temperature range −140–150 °C. Thermogravimetric analyses (TGA) were carried out under nitrogen with a Setaram 92-12 apparatus, at a heating rate of 5 °C/min between 25 and 1000 °C. Gel permeation chromatography (GPC) was performed with Waters columns (Styragel HR3 and 10^4 Å), refractive index and UV detection, using THF as eluent and polystyrene (PS) standards. The values of average molecular weights thus obtained were corrected by a factor of 0.67, taking into account the well-known fact that PS calibrated GPC measurements overestimate the real molecular weights of aliphatic polyesters [14].

Table 1
Characterization of the furan monomer HMFAE

IR (KBr pellet) cm^{-1}		^1H NMR (in CD_2Cl_2)					UV (in CH_2Cl_2)	
				δ (ppm)	*i*	*J* (Hz)	λ_{max}	308 nm
CH (furan)	3121	H_1	Singlet	3.57	1		ε	30,000 $l\ mol^{-1}cm^{-1}$
OH	3435	H_2	Singlet	4.57	2			
CH_3	2981	H_3	Doublet	6.36	1			
CH_2	2936–2872	H_4	Doublet	6.57	1			
C=O	1707	H_5	Doublet	7.38	1	15.42		
C=C	1636	H_6	Doublet	6.27	1	15.76		
Furan ring	1020	H_7	Quadruplet	4.23	2			
CH=CH trans	969	H_8	Triplet	1.31	3			

Thermal analysis	Elemental analysis			
		%C	%H	%O
$T_g = -53$ °C	Calculated	61.22	6.12	32.65
$T_c = -8$ °C	Found	59.10	6.20	33.80
$T_m = 33.5$ °C				

2.6. Irradiation procedure

The irradiations were carried out in a nitrogen atmosphere using a 500 W medium-pressure mercury arc provided with a Pyrex filter, to limit the excitation to wavelengths higher than 270 nm.

The intensity of UV light was about 5×10^{-9} Einstein s^{-1} cm^{-2}. Since, the kinetics was followed and the photo-curing was accomplished with different times, it was decided to give the UV light intensity rather than the UV-dose, which is time dependent.

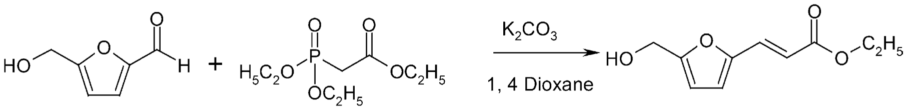
2.7. Contact angle measurements and surface energy determination

Drops of water, formamide and *n*-hexadecane were placed on the irradiated films and their contact angles measured using the home-made apparatus previously described [15]. The data were then treated following the classical approach proposed by Owens and Wendt [16] to obtain the dispersive and polar contributions to the polyester surface energy.

3. Results and discussion

3.1. Synthesis and characterization of HMFAE

The furan monomer was prepared by the Wittig–Horner reaction [17] between HMF and triethylphosphonoacetate (TEP):



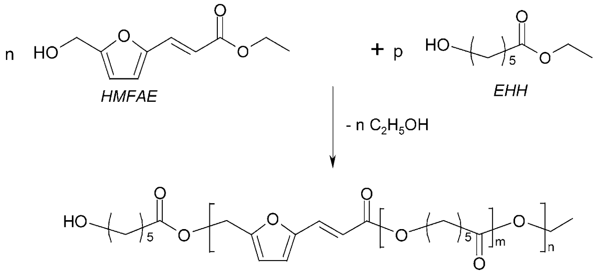
HMF **TEP** **HMFAE**

The use of TEP, instead of the corresponding phosphoranes typically used in conventional Wittig reactions, had the advantage of being less expensive and more water soluble, which facilitated its separation from the product. The characterization of HMFAE is given in Table 1 and showed good agreement with literature data [13]. The *trans*-configuration of the double bond external to the furan ring was established unambiguously by FTIR, through the presence of the characteristic peak at 969 cm^{-1}, and by ^{1}H NMR through the coupling constant of 16 Hz for the double bond protons.

3.2. Synthesis and characterizations of the copolymers

The furan chromophore was inserted into a copolyester backbone by copolytransesterification of HMFAE with EHH. This monomer combination was motivated by the fact that the aliphatic structures provide the film forming properties thanks to their long alkyl chains, whereas the conjugated furan units constitute the photocross-linking moieties. Indeed, our previous study of the photochemistry of HMFAE [18] showed that it readily dimerises under near-UV irradiation through a $[\pi 2+\pi 2]$ molecular coupling.

The copolymerisations were conducted at relatively modest temperatures, since the Fu–CH=CH moiety is sensitive to thermal treatment which induces branching reactions involving the furan ring and the double bond [12]. The reaction medium was also protected from the laboratory light, because of the photosensitivity of the furan structures. The reactions were carried out using K_2CO_3 as the catalyst, because of the negative effect on the furan heterocycle of transition-metal compounds, such as $Ti(OBu)_4$, frequently used in this type of reaction. Indeed, it was found [12] that the furan ring and $Ti(OBu)_4$ form a complex which traps the transition metal and impedes its catalytic role.



Numerous polycondensations were carried out using different experimental conditions, as summarized in Table 2, which collects the data related to the most relevant runs.

The percentage missing with respect to 100% yield was attributed to oligomers soluble in methanol. The polydispersity of these copolyesters was within the expected value for a linear polycondensation.

The structure of the copolymers was determined by ^{1}H NMR spectroscopy (Fig. 1). The furan units of all copolymers displayed the same *trans*-configuration borne by the monomer, as confirmed by FTIR and ^{1}H NMR spectroscopy. The signal assignments, made on the basis of chemical shifts and peak multiplicities, are resumed in Table 3. The formation of new bonds among aliphatic and furan units resulted in the appearance of three peaks. The signal at 5.16 ppm (H_α) represented the CH_2 protons between two furan units, that at 5.05 ppm (H_β), the CH_2 protons between an aliphatic and a furan unit and that at 4.15 ppm (H_γ), the CH_2 protons between two aliphatic units. Thus, the percentage of furan units in the copolymer could be calculated using the following equation:

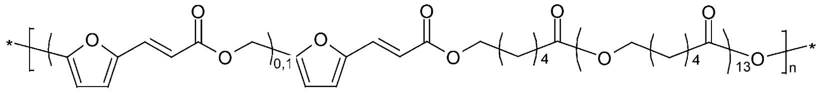
Table 2
Experimental data related to a number of polycondensations carried out under different conditions

Experiment number	Experimental conditions	Reaction time (h)	Yield (%)	$\bar{M}_W$	$\bar{M}_n$
1	95 °C, 7 mol% $\text{HMFAE}_{\text{initial}}$	20	75	3770	1640
2	95 °C, 20 mol% $\text{HMFAE}_{\text{initial}}$	20	73		
3	95°C, 50 mol% $\text{HMFAE}_{\text{initial}}$	30	60		
4	120 °C, 10 mol% $\text{HMFAE}_{\text{initial}}$	20	78	4724	2120
5	120 °C, 10 mol% $\text{HMFAE}_{\text{initial}}$	60	85	6818	2854
6	95 °C, 10 mol% $\text{HMFAE}_{\text{initial}}$	60	70		

$$\%\text{Fu} = \frac{i_{H_\beta} + i_{H_\alpha}}{i_{H_\beta} + i_{H_\alpha} + i_{H_\gamma}}$$

where i_{H_x} is the intensity of the X proton integral.

As an example, the copolymer obtained in experiment **5** (Table 2) had the following structure:



i.e. it contained about 8% in moles of furan units.

As shown in Table 4, for all the copolyesters, i_{H_γ} was higher than i_{H_β}, i.e. the furan monomer was found to be less reactive than its aliphatic homologue by a factor of about 20. Khrouf et al. [12] found similar results with other combination of furan and aliphatic monomers in copolymerisations by transesterification. This also explains the very low value of i_{H_α} considering moreover that the initial proportion of HMFAE in the reaction mixture was purposely low. However, an increase in reaction temperature favored the insertion of the furan monomer, as shown by the results of runs **4** and **5**.

The incorporation of HMFAE units in the copolymer reached a plateau with reaction time, as illustrated in Fig. 2, which shows that after about 30 h, it became impossible to insert more furan units.

The UV spectrum of the copolymers (Fig. 3) showed a maximum at 308 nm, viz. the same as that of the furan monomer, which suggested that the furan chromophore moiety was not involved in any side reaction during the polycondensation. This was confirmed by the fact that $\bar{M}_w$ grew linearly with reaction time (Fig. 4), as expected for a linear polycondensation, excluding the occurrence of branching reactions arising from the external unsaturation of HMFAE.

The DSC traces (Fig. 5) showed that the copolyesters displayed a fairly high degree of crystallinity and their glass transition only appeared after quenching the heated samples

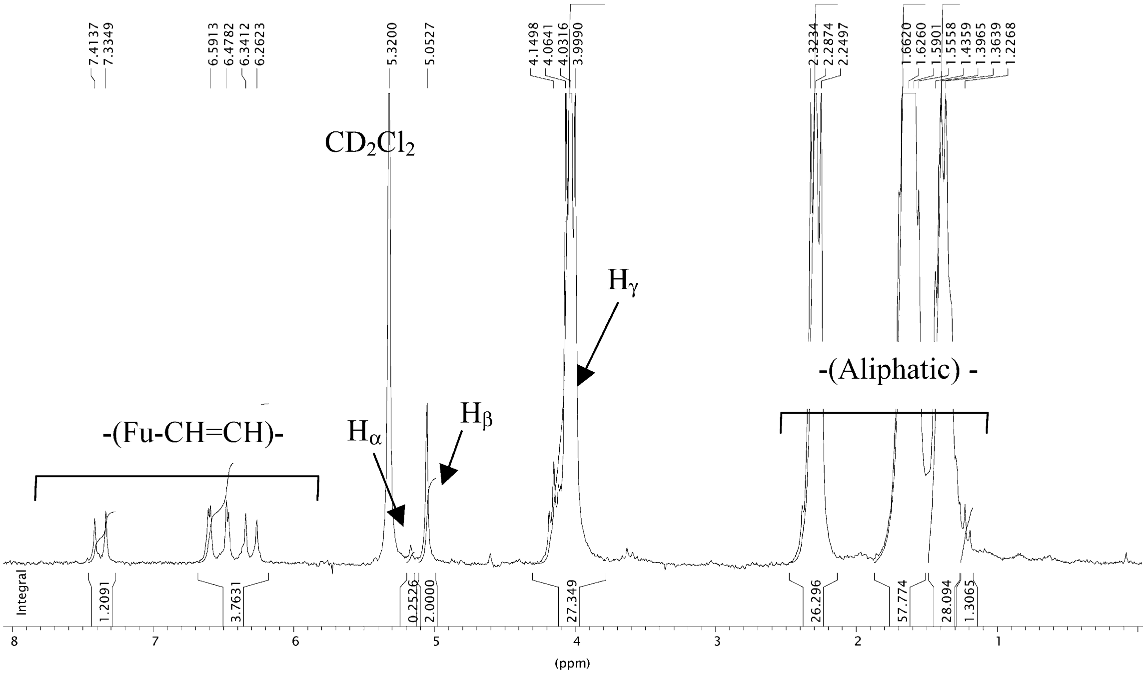


Fig. 1. ^{1}H NMR spectrum of copolymer **5** in CD_2Cl_2.

Table 3
Characterization of copolymer **5**

IR (KBr pellet) (cm^{-1})		^1H NMR (in CD_2Cl_2)					UV (in CH_2Cl_2)	
				δ (ppm)	i	J (Hz)	λ_{max}	308 nm
OH	3429	H_α	Singlet	5.16	0.25			
CH_2	2950–2873	H_β	Singlet	5.05	2		ε	2700 l $mol^{-1}cm^{-1}$
C=O	1711	H_γ	Singlet	4.15	27			
C=C	1637	$H_{Fu\text{–}CH=CH\text{–}}$	Several doublets	7.41	5	15.76		
Furan ring	1017	$H_{aliphatic}$	Multiplet	2.32	112	15.76		
CH=CH trans	969							

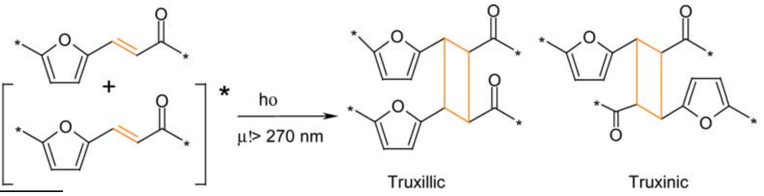
Solubility		Thermal analysis	Elemental analysis			
				%C	%H	%O
Hexane	2 Phases	$T_g = -52$ °C	Calcd	63.70	8.28	28.65
Acetone	Soluble	$T_c = -34$ °C	Found	61.47	8.02	27.93
Dichloromethane	Soluble	$T_m = 44$ °C				
Ether	Insoluble	Thermogravimetric analysis				
Alcohol	Insoluble	$T_d = 225$ °C, $\delta = 85\%$				
THF	Soluble					

in liquid nitrogen, together with the recrystallisation of the amorphous polymer above T_g (Tables 4 and 5). The growing presence of furan monomer units in the copolymer resulted in a progressive decrease in the extent of crystalline domains (calculated from the area per unit mass of the melting peak and taking $\Delta H_f = 139$ J g^{-1} as the melting enthalpy of the aliphatic polyester [19]), as shown in Table 5. Conversely, T_g increased linearly with the furan monomer content in the copolymers (Fig. 6), as expected for random structures and from the fact that the furan units had a much stiffer structure than the aliphatic ones.

The TGA traces (Fig. 7) showed that these materials were stable up to 225 °C, after which they started degrading with a final weight loss of 80–90%. These copolymers displayed the same behavior as that of the pure aliphatic polyester, i.e. polycaprolactone, which is known to be stable up to 250 °C and then to suffer typical ester thermolyses, losing 100% of its weight [20]. For our copolymers, the carbonaceous residue was obviously associated with the presence of the furan moieties, which are known to graphitize at high temperature when present in macromolecular structures [21].

3.3. Photochemistry

Our recent study of the photochemistry of HMFAE [18] suggested that the near-UV irradiation of the copolymers should induce intermacromolecular couplings between an excited and a ground-state furan chromophore, viz.:



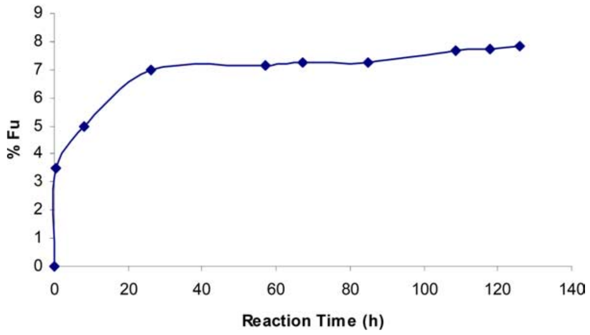


Fig. 2. Extent of furan monomer incorporation as a function of the reaction time for experiment **5**.

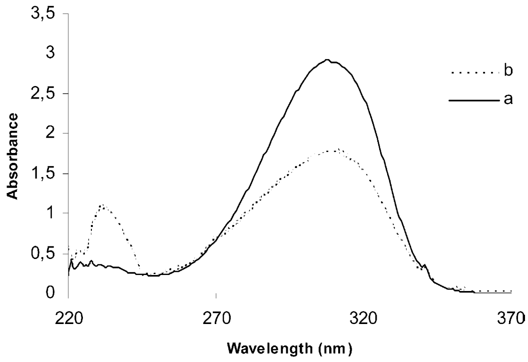


Fig. 3. UV spectrum of copolymer **5** (a) and of the soluble oligomer isolated after its short irradiation (b), both in spectrophotometric CH_2Cl_2.

Table 4
Furan monomer contents in the copolymers.

Experiment number	i_{H_α}	i_{H_γ}	%Fu
1	0	50	3.9
2	0.6	10	9.8
3	1.6	8	33
4	0	34	5.4
5	0,2	26	7.6
6	0	40	4.6

Table 5
Glass transition, crystallization, melting temperatures and crystallinity of the copolymers as a function of the furan monomer content.

%Fu	T_g (°C)	T_c (°C)	T_m (°C)	Crystallinity (%)
0	−51.5	None	71.5	82.2
2.4	−62.2	None	51.1	71.9
3.9	−61.7	−43.9	55.3	Nc
4.6	−58.2	−40.5	48.9	63.8
6	−56.0	−38.4	50.7	61.2
7.6	−52.3	−34.4	44.3	49.3

eventually leading to the formation of a polymer network. In other words, it was expected that the same coupling mechanism should applied to both HMFAE and its corresponding moieties within the copolymers.

A first piece of evidence in favour of this mechanism was obtained by following the irradiation by FTIR spectroscopy. Fig. 8 shows that the most relevant change was, as expected, the progressive decrease of the alkenyl C=C peak at 1640 cm^{-1}, which was accompanied by the appearance of peaks corresponding to the cyclo-butane ring, near 1200 cm^{-1} for CH bending and near 735 cm^{-1} for the ring deformation. Understandably, these spectral changes were quantitatively much less important than those observed with HMFAE [18], because of the lower probability of binary chromophore encounters, compared with the bulk monomer, arising from (i) the low concentration of furan chromophores in the copolymers, and (ii) the lower mobility of the polymer chains. Thus, it took between 20 min and 2 h to reach 50–60% of coupling, depending on the furan unit content in the copolymer, and thereafter the rate of double bond consumption decreased drastically, suggesting the formation of networks in which the chain mobility was drastically hampered.

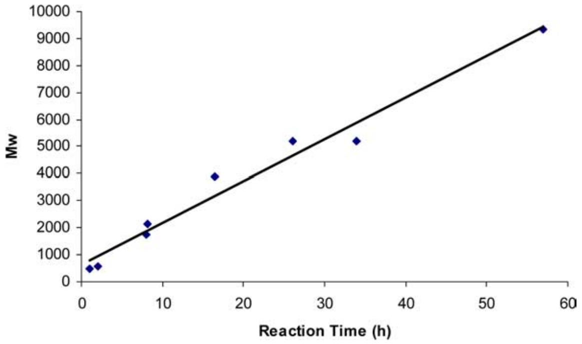


Fig. 4. Evolution of $\bar{M}_W$ with the reaction time for experiment **5**.

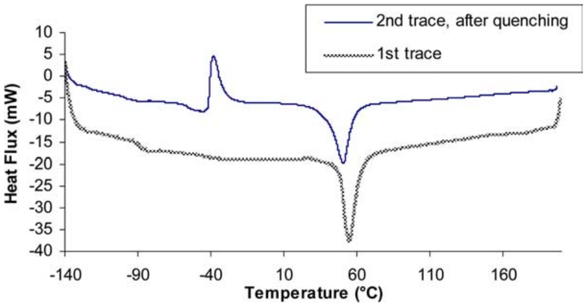


Fig. 5. DSC traces of copolymer **5**.

Irradiation of the films was followed by a soxhlet extraction with methylene chloride. The soluble portions displayed ^{1}H NMR and FTIR spectra similar to those of the initial copolymers, except for the fact that the peaks relative to the alkenyl unsaturations were less intense, suggesting the presence of branched structures arising from partial photocoupling among the original linear macromolecules. Their UV spectra showed the peak at 308 nm for the unreacted furan monomer units and a new peak at 232 nm (Fig. 3), attributed to the unconjugated furan rings of the coupled moieties [18]. In the FTIR spectra of the insoluble residues the relative intensity of those peaks was very small, indicating that most unsaturations had been involved in the network formation. The extent of cross-linking for 50 μm thick films irradiated for 4 h, as determined by the mass balance after each extraction, depended on the amount of furan chromophores present in the copolymer and was found to be 78, 67 and 59% for samples **5**, **4** and **6**, respectively.

These relatively low cross-linking efficiencies were attributed mainly to the excessive thickness of the films, compared with the typical values associated with photosensitive coatings in offset plates, namely a few micrometers. Moreover, under industrial conditions, the energies applied during irradiation are much higher. It appears, therefore,

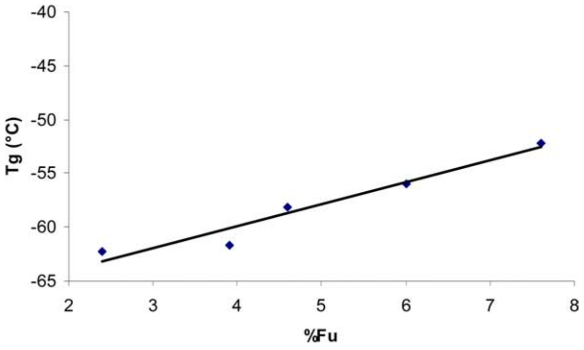


Fig. 6. Evolution of the T_g of the copolymers as a function of the furan monomer content.

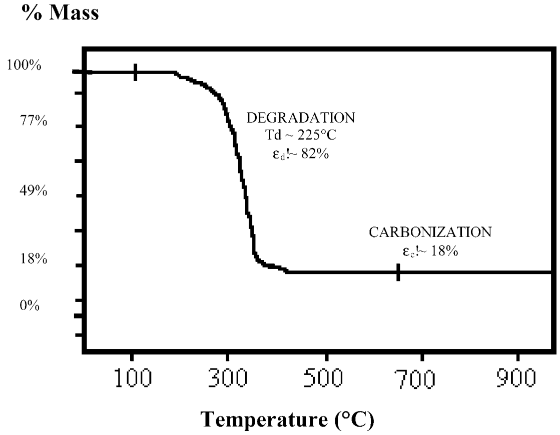


Fig. 7. TGA trace of copolymer **5**.

that these materials are not far from reaching the possibility of application. The use of a photosensitizer was tested, but the results suggest that a more systematic study is necessary in this context.

When the copolymers, which were in their *trans* conformation, were irradiated in dilute media (very low intermolecular collision rate), they underwent a progressive unimolecular *trans–cis* isomerization [18] to reach the equilibrium concentration of conformers, as shown by FTIR spectroscopy (Fig. 9), where a peak characterizing the *cis* isomer appeared at 820 cm^{-1} and its intensity increased with time to reach a constant value, reflecting the onset of the *cis–trans* equilibrium. However, the rate and the extent of the conversion was less pronounced than with HMFAE [18], most probably because of the steric hindrance associated with rotational movements of the excited chromophore units in the copolymer.

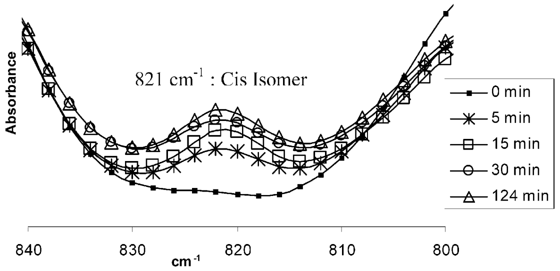


Fig. 9. FTIR spectrum (in spectrophotometric CH_2Cl_2) of the soluble part of irradiated copolymer **5**.

3.4. Surface energy

The value of the total surface energy of the cross-linked polymers was found to be 37 mJ m^{-2}, with dispersive and polar contributions of 26 and 11 mJ m^{-2}, respectively. These values are in tune with the typical requirement of negative photosensitive offset coatings after development, in terms of their ability to allow fast ink spreading.

4. Conclusion

This study showed the possibility of inserting furan chromophores in an aliphatic polyester structure by transesterification copolymerisation under mild experimental conditions. Thus, semicrystalline copolyesters with up to 10% of furan units were obtained in bulk, without excessive

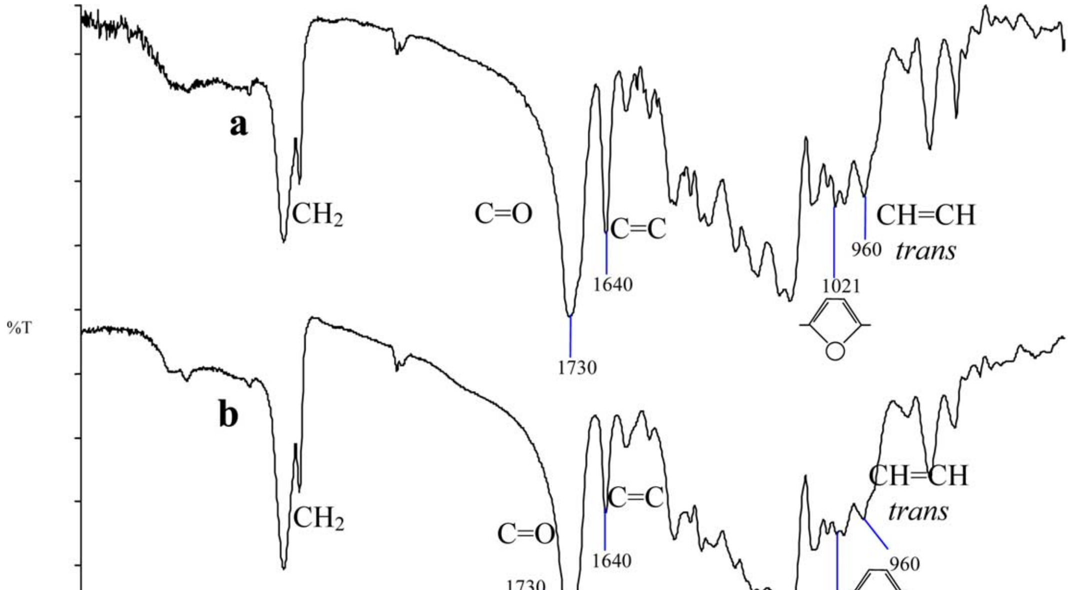


Fig. 8. FTIR spectra of copolymer **5** before (a) and after 2 h (b) of irradiation in a KBr pellet.

heating. Their UV spectrum showed a maximum at 308 nm, as in the case of the furan monomer.

When they were irradiated with near-UV light, they followed the classical molecular photocycloaddition mechanism of cinnamic derivatives, giving insoluble networks. This makes them good candidates for negative photoresist applications. Work is in progress to enhance their photo-cross-linking rate through the use of photosensitisers.

Acknowledgements

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