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NEW FUNCTIONALIZATION METHOD FOR RADIATION CURABLE POLYURETHANES CONTAINING PENDANT ACRYLATE GROUPS

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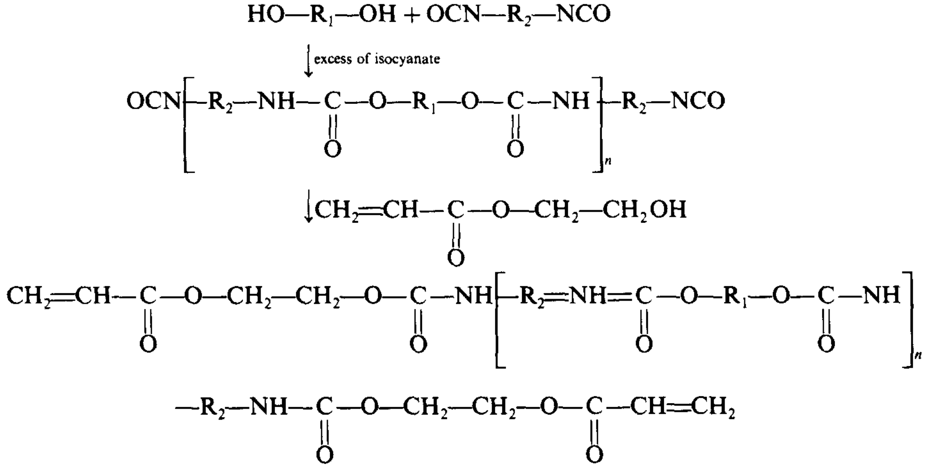
Abstract—Polyurethane oligomers, with pendant acrylic groups useful in photocrosslinkable systems, were synthesized by a new way of functionalization, convenient for attaining a higher functionality of acrylic groups. They were used as base components for curable formulations; their reactivity and physical properties were studied by comparison with classical systems.

INTRODUCTION

Photocrosslinkable systems used in coating technology generally consist of an oligomer with polymerizable end-position groups and a reactive diluent. The present work concerns the synthesis and the evaluation of new polyfunctional polyurethane oligomers with pendant acrylic groups.

Acrylic polyurethane oligomers useful as bases in formulations for coatings are generally obtained by reaction of 2-hydroxyethyl acrylate (HEA) on an oligomer with isocyanate end-groups:



$$HO{-}R_1{-}OH + OCN{-}R_2{-}NCO$$

$$\Big\downarrow \text{excess of isocyanate}$$

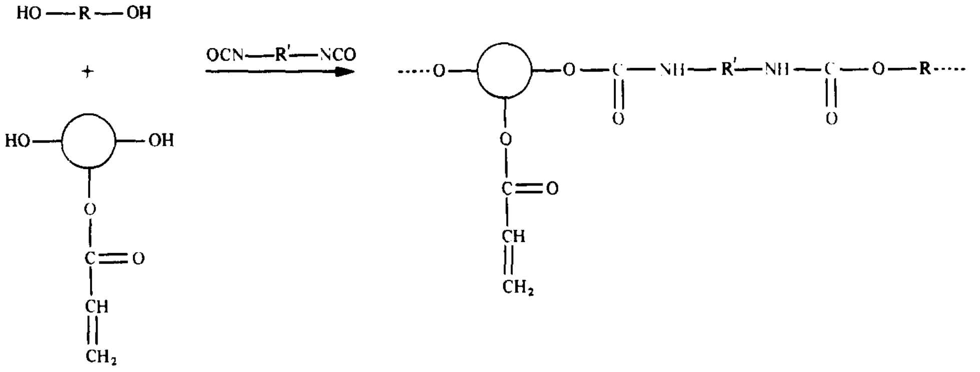
$$OCN\left[-R_2-NH-\underset{\underset{O}{\|}}{C}-O-R_1-O-\underset{\underset{O}{\|}}{C}-NH\right]_n-R_2-NCO$$

$$\Big\downarrow CH_2{=}CH-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2OH$$

$$CH_2{=}CH-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-NH\left[-R_2{=}NH{=}\underset{\underset{O}{\|}}{C}-O-R_1-O-\underset{\underset{O}{\|}}{C}-NH\right]_n$$

$$-R_2-NH-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-CH{=}CH_2$$

Recent work [1] has been carried out to introduce acrylic groups in side positions to lead to a higher functionality. We have investigated the possibility of using a dihydroxylated acrylic ester in polycondensation:



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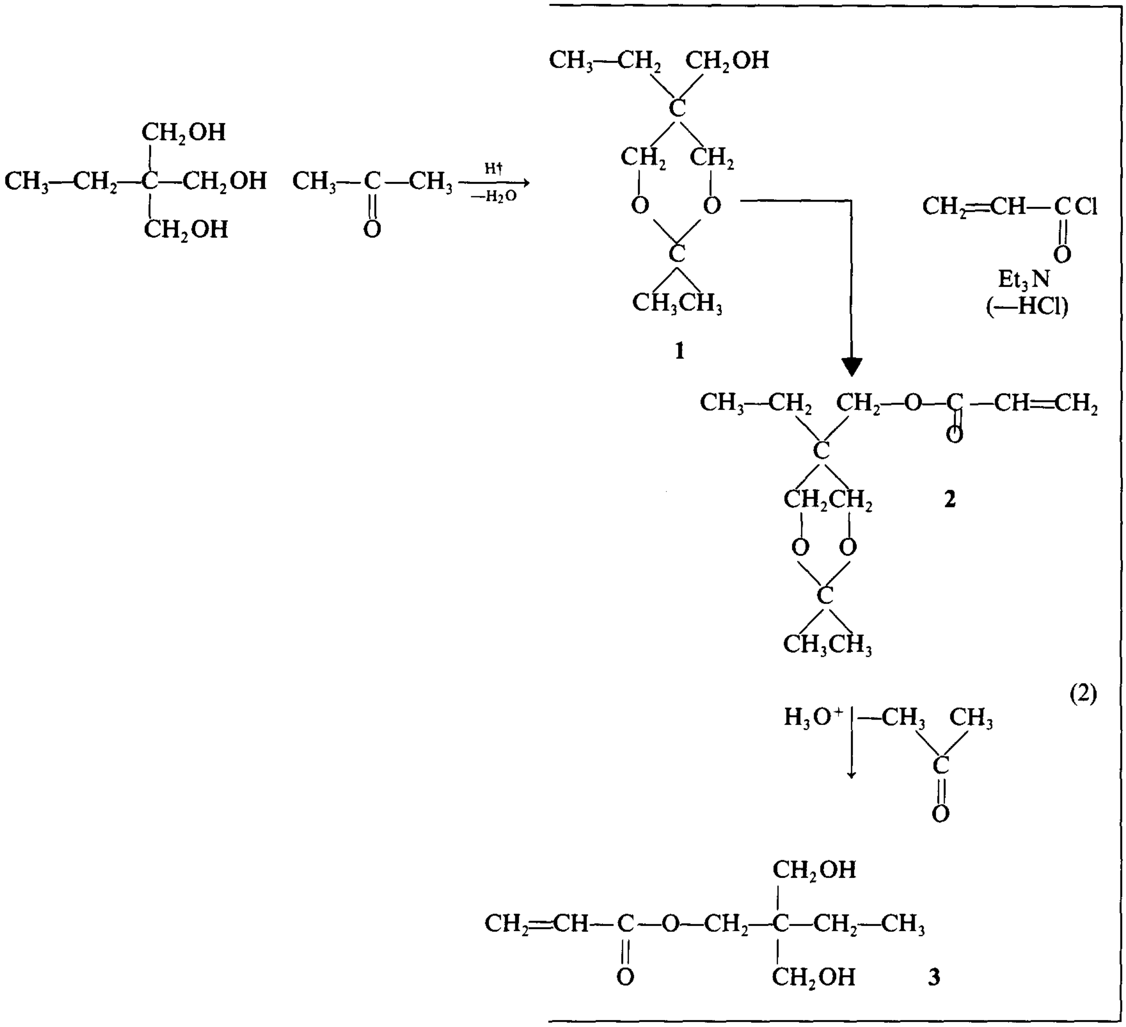
The oligomer functionality then depends on the molar fraction of the acrylic diol in the mixture of diols, and on the ratio [alcohol]/[isocyanate] that determines the molecular weight of the resulting oligomer.

The possibility of attaining a functionality greater than two leads, after photoreticulation, to a higher network density giving a material with better physical characteristics (hardness, abrasion, chemical resistance, etc.).

In this paper we describe the use of acrylic monoester of 2,2-dihydroxymethyl butylacrylate (TMP, trimethylolpropane) 3, the synthesis of which is conducted thus:



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EXPERIMENTAL PROCEDURES

Solvents were purified by classical methods; triethylamine and acryloyl chloride were distilled before use.

Synthesis of 5-ethyl 5-hydroxymethyl 2,2-dimethyl 1,3-dioxolane (1)

1 was prepared by a method previously described for glycero [2], with 1 g of *p*. toluene sulphonic acid per mol of TMP. Distillation of the crude product gave **1** with 80% yield (b.p.$_{5\,\mathrm{mm}}$ = 115°).

Synthesis of 5-acryloyloxymethyl 5-ethyl 2,2-dimethyl 1,3-dioxolane (2)

Acrylic ester of **1**, synthesis of which by transesterification has been described [3], was obtained by reaction of acryloyl chloride with **1** in dichloromethane at 0° with triethylamine as HCl captor. After filtration, the resulting mixture was washed with an equivolumetric solution of 5% aq. HCl and then with pure water. The organic phase was dried with $MgSO_4$ and the solvent removed. The crude product was distilled under reduced pressure and **2** was obtained as a colourless liquid in 75% yield (b.p. at 0.8 mm Hg = 59°, CPV purity = 97%).

Hydrolysis of the acetal

The reaction was carried out at 60° by stirring **2** vigorously with 0.5 N aq. HCl for *ca* 1 hr, after which the emulsion become a limpid solution, cooled at room temperature. The product was extracted with dichloromethane and the solution neutralized with K_2CO_3. After filtration and removing the solvent, the product was dried with $MgSO_4$ and stored over 4 Å molecular sieve ($H_2O < 3\%$).

Reaction of isocyanates

The acrylic diol, **1**, was disolved in toluene to give 0.25 mol · l^{-1} and heated to 50°. Then the corresponding stoichiometric amount of isocyanate was rapidly added and the temperature maintained at 50°. The progress of the reaction was followed by reaction with an amine on a sample (formation of urea) and potentiometric estimation of the excess amine [4].

Polyurethane formation

The diol or the mixture of diols was heated at 60° under inert atmosphere; the di-isocyanate was then rapidly added and the mixture vigorously stirred in the presence of 0.2 g of stannic dibutyldilaurate as catalyst. The temperature was maintained at 60° until the residual isocyanate, determined as above, was lower than $1 \cdot 10^{-2}\,mol \cdot kg^{-1}$ (around 5 hr).

Photo-initiated polymerization

The photo-initiated bulk polymerization was carried out as previously described [5]. The formulation containing 5% weight of 2,2-dimethoxyphenyl acetophenone (Irgacure 651 from CIBA-GEIGY) as photo-initiator was applied as a 25 μm thick film on a NcCl disc. The sample was irradiated at room temperature in the presence of air by a 700 W hg-vapour lamp, the radiation of which was concentrated by a semi-elliptical reflector. The irradiance (energy received by the sample), measured by a radiometer with a spectral window of 250–400 nm, was $146\,mW \cdot cm^{-2}$. A mechanical camera shutter provided exposure times in the range $1 \cdot 10^{-2}$ to 1 sec. The progress of the reaction was determined by i.r. spectrometry by monitoring the decrease of the $810\,cm^{-1}$ absorption band (twisting vibration) of the acrylic double bond, corrected by means of a reference band [5].

RESULTS AND DISCUSSION

Reaction of isocyanates

A kinetic study of the reaction of **3** with various isocyanates [equation (3)] was carried out to evaluate its reactivity in polyurethane formation. Figure 1 shows the progress of the reaction against time, for a few isocyanates. The reaction of HEA with butyl isocyanate was also carried out for comparison.

The reaction was carried out in toluene at 50° to prevent the polymerization of acrylic groups. As expected, the reaction with aromatic isocyanates is faster than with aliphatic. The 2nd order kinetic constants of the reaction show that HEA is a little more reactive than 2,2-dihydroxymethyl butyl acrylate (**3**).

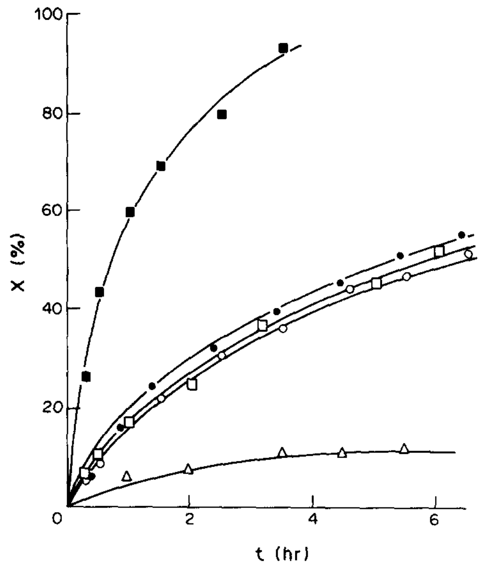


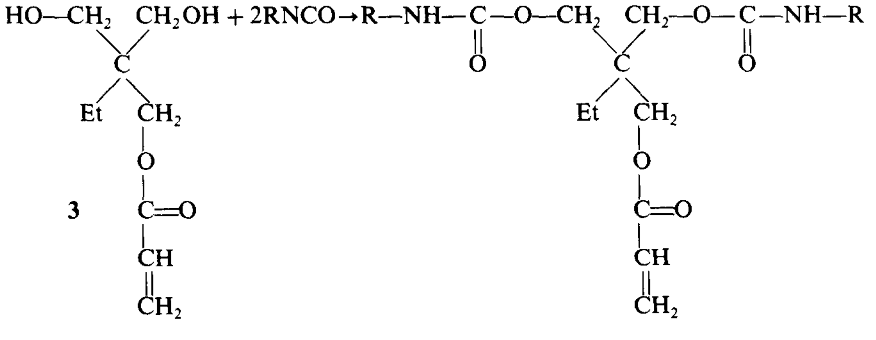
Fig. 1. Kinetics of the reaction of **3** with phenyl isocyanate (■), 1,6-hexyl di-isocyanate (●) butyl isocyanate (○); of **4** with butyl isocyanate (□); and of **5** with butyle isocyanate (△) in toluene at 50°.

Under the same conditions, the reaction is isocyanates with a hydroxytelechelic polypropylene glycol (PPG) (**5**) ($\bar{M}_n = 490$), was slower, probably because of the mobility of the hydroxyl groups.

Synthesis of oligomers polyurethanes with pendant acrylic groups

Because of this difference in reactivity, the formation of a polyurethane by reaction of a mixture of the acrylate diol **3** and the PPG with a diisocyanate suggests that the acrylic groups will be in central positions in the chain. Because of the necessity of limiting the molecular weight for the purpose of use in formulations ($\bar{M}_p \approx 2000$), the number of constitutive units is very small (3–5). In this case, the distribution of the acrylic groups attached to the main chain can be considered to be statistical.

The main characteristics of the oligomer samples synthesized with hexamethylene diisocyanate (HMDI) are indicated in Table 2, in comparison with



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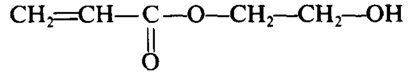
(3)



$$CH_2{=}CH{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}OH$$

4

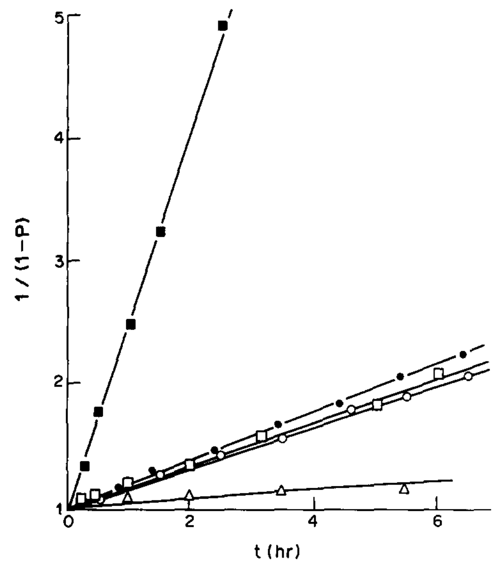


Fig. 2. Determination of rate constants (for legend—see Fig. 1).

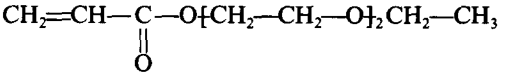
a commercial one (Actilane 20 from SNPE). $\bar{M}_n$ values were determined by GPC; the average functionality and the ratio of acrylic groups in mol · kg^{-1} are calculated from the stoichiometric amounts.

Table 1. Rate constants of the reaction of **3**, **4** and **5** with butyl isocyanate (BuNCO), phenyl isocyanate (PhNCO), and hexyl diisocyanate (HMDI); conditions of reaction: see Fig. 1

Alcohol	Isocyanate	k(mol^{-1} l · hr^{-1})	No.
	PhNCO	2,48	**1**
3	BuNCO	0,29	**4**
	HMDI	0,40	**2**
4	BuNCO	0,64	**3**
5	BuNCO	3.10^{-2}	**5**

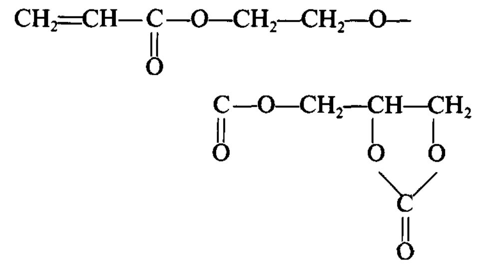
The monomer **7** is one of the family of monomeric carriers of cyclic carbonate function the great reactivity of which in photo-initiated polymerization has been demonstrated [6, 7].

(EDGA)



$$CH_2{=}CH{-}\underset{\overset{\|}{O}}{C}{-}O\!\left[CH_2{-}CH_2{-}O\right]_2CH_2{-}CH_3$$

6



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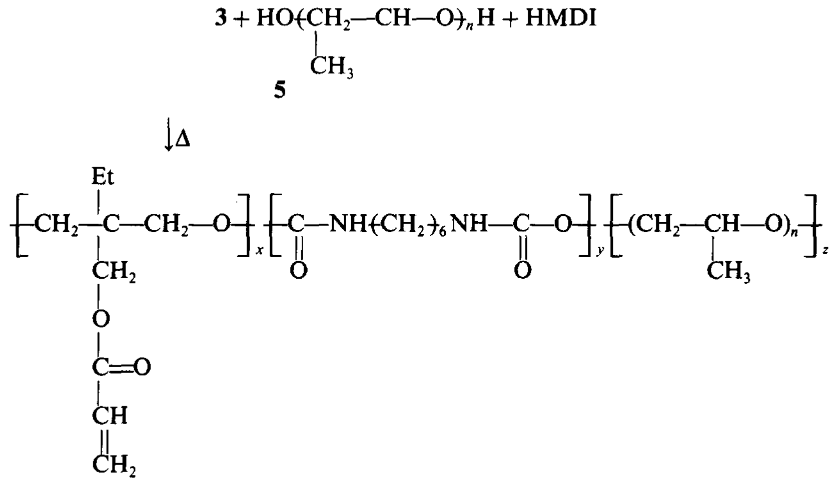

(4)

Photoreticulation

The formulations tested in bulk photo-initiated polymerization consisted of:

- —50 parts by weight of acrylic-functionalized oligomer;
- —50 parts by weight of reactive diluent;
- —5 parts by weight of photo-initiator Irgacure 651 (see Experimental Procedures).

The monofunctional acrylic monomers used as reactive diluents **6** and **7** allow the viscosity of the mixture to be adapted to experimental conditions, and are incorporated into the network during polymerization.

Conversion curves (Fig. 3) of formulations containing ethyl-diglycol acrylate (EDGA) **6** as diluent monomer show that, for an equivalent initial acrylic group ratio, the higher functionality of the oligomer involves a lower reactivity of the formulation, unlike the effect of a higher functionality of the diluent monomer, probably because of the higher density of the network formed during irradiation that decreases the accessibility of the unsaturations.

With much more functionality (formulation No. 3) and a very reactive diluent, the effect of the network density is to increase the residual unsaturation ratio (around 10%).

Table 2. Characteristics of polyacrylic polyurethane oligomers used as bases of formulations; molar fractions: x, **3**; y, HDMI; z **5**; $[A]$, acrylic unsaturations ratio; $\bar{f}$, average acrylic groups functionality

No.	x	y	z	$\frac{[OH]}{[NCO]}$	$[A]$ (eq. kg^{-1})	$\bar{M}_n$	$\bar{f}$
1	Actilane 20				1,63		2
2	0.32	0.28	0.40	1.50	1.47	1500	2.6
3	0.57	0.43	—	1.33	3.94	1400 1600	4

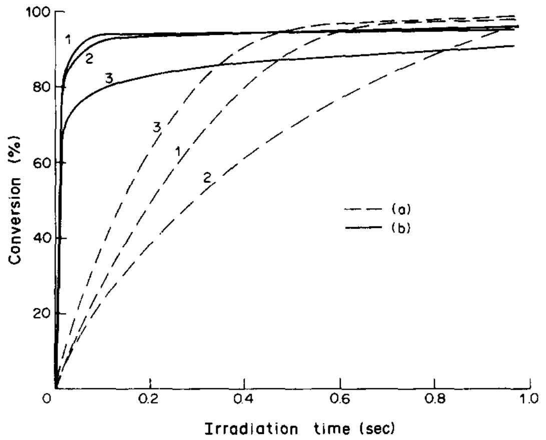

Fig. 3. Photoreticulation of formulations containing polyacrylic polyurethane oligomers; **1**, **2** and **3**: see Table 3; (a) diluent **6**, (b) diluent **7**; irradiance: 146 mW · cm^{-2}.

Table 3. Photoreticulation of polyurethane polyacrylic formulations; **1**, **2** and **3**, see Fig. 3; $[A]_0$, initial concentration of acrylic groups; R_p, maximal rate of photopolymerization; δ, residual acrylic unsaturations ratio

	Diluent **6**			Diluent **7**		
Oligomer	$[A]_0$	R_p	$\delta(\%)$	$[A]_0$	R_p	$\delta(\%)$
1	3.31	7	3	2.61	113	5
2	3.23	7.3	2	2.53	99	5
3	4.41	17	3	3.71	148	10

$[A]_0$, eq · kg^{-1}. R_p, eq · kg^{-1} sec^{-1}.

Superficial hardness

Superficial PERSOZ hardness measurements of the resulting coatings were carried out and plotted against the irradiation time (Fig. 4). As expected, the higher functionality of the oligomers and consequently the crosslinking density lead to a greater hardness of the coating, with the disadvantage of a decrease in the polyurethane character of the network formed.

CONCLUSION

The formation of a network by crosslinking acrylic groups attached to a polyurethane chain gives a material with the physical and mechanical properties needed in coatings technology, establishing a compromise between hardness and flexibility, depending on the polyurethane/polyacrylic nature of the network.

The distribution of acrylic groups along the polyurethane chain gives a more homogeneous network involving better physical properties, with a lower residual unsaturation ratio than found for a polyfunctional diluent, which can have a negative effect on weathering.

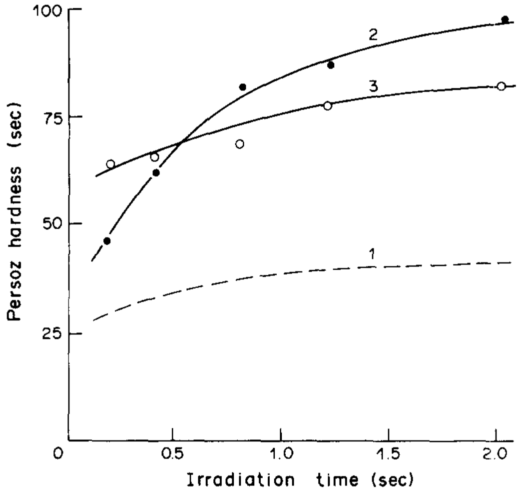

Fig. 4. Evolution of superficial hardness of photoreticulated films containing polyacrylic polyurethane oligomers; **1**, **2** et **3**: see Table 3.

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