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Unsaturated modified poly(vinyl alcohol). Crosslinking through double bonds

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Abstract

Poly(vinyl alcohol) (PVA) was esterified with 10-undecenoyl chloride to give polymers with different degrees of modification which were studied in order to find how the concentration of reactive sites can influence the crosslinking process. The polymers obtained were characterized by spectroscopic techniques, elemental analysis and thermal methods. Weight average molecular weights and viscosities were determined. Thermal crosslinking of the double bonds on the side chain took place in all cases, but was overlapped by the degradation process. Thus, dicumyl peroxide had to be used to obtain the cured material and avoid degradation. Activation energies for radical initiated crosslinking were determined by means of dynamic DSC studies. Isoconversional kinetic analysis was applied to DSC data and the dependences of activation energies on conversion degrees were obtained and compared with those obtained from polymers with the same pendant chain but a more flexible polyether main chain. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl alcohol); Crosslinking; Thermoset

1. Introduction

Chemical modification is a powerful tool for obtaining polymers with new properties and therefore for increasing the scope of their applications. The poly(vinyl alcohol) (PVA) is the only polyvinyl-type synthetic polymer which has been confirmed to be biodegradable [1]. This feature and its water solubility infer the advantage of easier degradation and elimination after use. Due to its biocompatibility, PVA can be used for a variety of biomedical applications, preferably in the form of hydrogel. It has been modified with different compounds such as aldehydes, carboxylic acid, anhydrides, etc., to increase membrane selectivity and fiber manufacture among other things [2–4]. In two previous papers [5,6] we have described the preparation of two series of crosslinked polymers derived from PVA. In one of these papers [5], hydroxyl groups of PVA were reacted with dianhydrides to obtain a network with a high number of polar groups.

To reduce the degree of crosslinking, in the second paper [6], PVA samples were partially esterified and the remaining hydroxyl groups were reacted with dianhydrides and diisocyanates.

A different approach has been used in this study to obtain tridimensional networks. Thus, PVA modified with a vinyl-terminated carboxylate enables its double bonds to be crosslinked. Because the crosslinking density is influenced by the number of reactive sites, 10-undecenoate esters of PVA with different degrees of esterification were obtained. Moreover, this long aliphatic chain spacer between the main chain and the reactive group introduces a great flexibility which makes the crosslinking reaction easier.

These polymers containing unsaturated units have potential for a wide range of applications including biodegradable elastomers, hydrogels and adhesives. Their crosslinking can improve their thermal and mechanical properties. Moreover, the unsaturated units can be converted into other functional groups, such as epoxy, carboxylic acid or hydroxyl group and all of these polymers can also be crosslinked.

Differential scanning calorimetry (DSC) was used to study the thermal properties of polymers and kinetic parameters involved in the crosslinking processes carried out initiated by dicumyl peroxide. In addition, thermogravimetry was used to test the thermal stability of polymers.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA) (Fluka) had a degree of hydrolysis of 86%. 10-Undecenoyl chloride (Fluka), 4-dimethylaminopyridine (DMAP) (Fluka), dicumyl peroxide (Aldrich), pyridine (Panreac), tetrahydrofuran (THF)

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(SDS), dichloromethane (SDS) and 1-methyl-2-pyrrolidone (NMP) (Fluka) were used as received.

2.2. Esterification reaction

PVA (0.05 mol) was dissolved by stirring in NMP (25 ml) and heating to 60–80°C. Different ratios of 10-undecenoyl chloride (OH/acyl group 1/1, 1/0.75 and 1/0.50), pyridine (0.05 mol) and DMAP (0.005 mol) were added at room temperature. Immediately a precipitate of the pyridinium salt was observed. The reaction was then stirred for 48 h at room temperature. The precipitate of pyridinium salt was removed by filtration and the polymer was obtained by precipitation into distilled water. The reaction product was purified by reprecipitating three times from THF into water, and then dried in vacuo at 50°C. The yields in the different reactions (OH/acyl group) were: (1/1) 78% (degree of esterification: 93 mol%, 10-undecenoate groups introduced 80%), (1/0.75) 73% (degree of esterification: 64 mol%, 10-undecenoate groups introduced 55%) and (1/0.50) 58% (degree of esterification: 45 mol%, 10-undecenoate groups introduced 39%).

2.3. Preparation of the samples for crosslinking by DSC

Samples were prepared by dissolving esterified PVA and dicumyl peroxide (5% w/w) in dichloromethane. Then, the solvent was removed under reduced pressure at room temperature. The mixtures were stored in the dark at 4–5°C. Approximately 5 mg samples of the mixture were weighed accurately in an aluminium DSC sample pan.

2.4. Instrumentation

^{1}H- and ^{13}C-nmr spectra were obtained using a Gemini 300 spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. IR spectra were recorded on a MIDAC GRAMS/386 FTIR spectrometer. Elemental analyses were carried out using a Carlo Erba 1106 device. Inherent viscosities (η_{inh}) were measured in 1-methyl-2-pyrrolidone (NMP)-solutions (ca. 2 g l^{-1}) at 30°C on a Schott–Geräte AVS 310 viscosimeter. SEC–MALLS measurements were made using a Waters 510 pump, a pre-column Shodex K-800P, a linear column Shodex K-80M (47 300 theoretical plates/m), a second linear column PLgel 5 μ MIXED-D (70 800 theoretical plates m^{-1}) and a third linear column PLgel 3 μ MIXED-E (97 200 theoretical plates m^{-1}) from Polymer Laboratories. Two detectors were used: a light-scattering MiniDAWN with laser photometer and a refractive index HP 1047 A from Hewlett Packard. Polystyrene standards were used for calibration of refractive index detector and the eluent was THF (Mallincrodt ChromAR HPLC).

Calorimetric studies were carried out on a Metler DSC-30 thermal analyzer in covered aluminium pans under nitrogen atmosphere at different heating rates (5, 10, 15 and 20°C min^{-1}). The calorimeter was calibrated using an Indium standard (heat flow calibration) and an Indium–Lead–Zinc standard (temperature calibration). Samples of a known weight (ca. 5 mg) of modified PVA with the initiator were put in an aluminium pan. T_g and the enthalpy of curing were determined in dynamic experiments. Isoconversional kinetic data were evaluated using the Mettler–Toledo TA 8000 kinetic software. Thermogravimetric analyses were carried out with a Perkin–Elmer TGA-7 system in N_2 at a heating rate of 20°C min^{-1}.

3. Results and discussion

The hydroxyl groups of the PVA were esterified by introducing crosslinkable pendant groups. This reaction was carried out from PVA with 10-undecenoyl chloride, pyridine and with 4-dimethylaminopyridine as catalyst. Two aprotic solvents, DMSO and NMP, were tested, but the latter gave higher degrees of modification.

In order to get the maximum degree of esterification two different PVA: acid chloride ratios (1:1 and 1:1.2) were

Table 1
Characterization of vinyl alcohol-vinyl 10-undecenoate copolymers (I, II and III)

	I	II	III
Ratio OH/acyl chloride	1/1	1/0.75	1/0.50
Elemental analysis (%)			
C	72.65	70.26	68.59
H	10.22	10.08	9.87
i.g. (%)	80	55	39
d.e. (%)	93	64	45
Inherent viscosity (g/dl)	0.22	0.28	0.32
$\bar{M}_w^a$	175 000	136 000	120 000
$\bar{M}_w^b$	126 963	98 120	79 661
$\bar{M}_w/\bar{M}_w^{est}$	1.4	1.4	1.5

i.g., Introduced groups (relating to 100 structural units of copolymer); d.e., degree of esterification (relating to OH groups); Inherent viscosity (NMP, 30°C), inherent viscosity of starting PVA 0.34 g dl^{-1}.

[a]Calculated by SEC.

[b]Calculated from the weight average molecular weight of starting PVA and the degree of substitution achieved assuming no side reactions occurred.

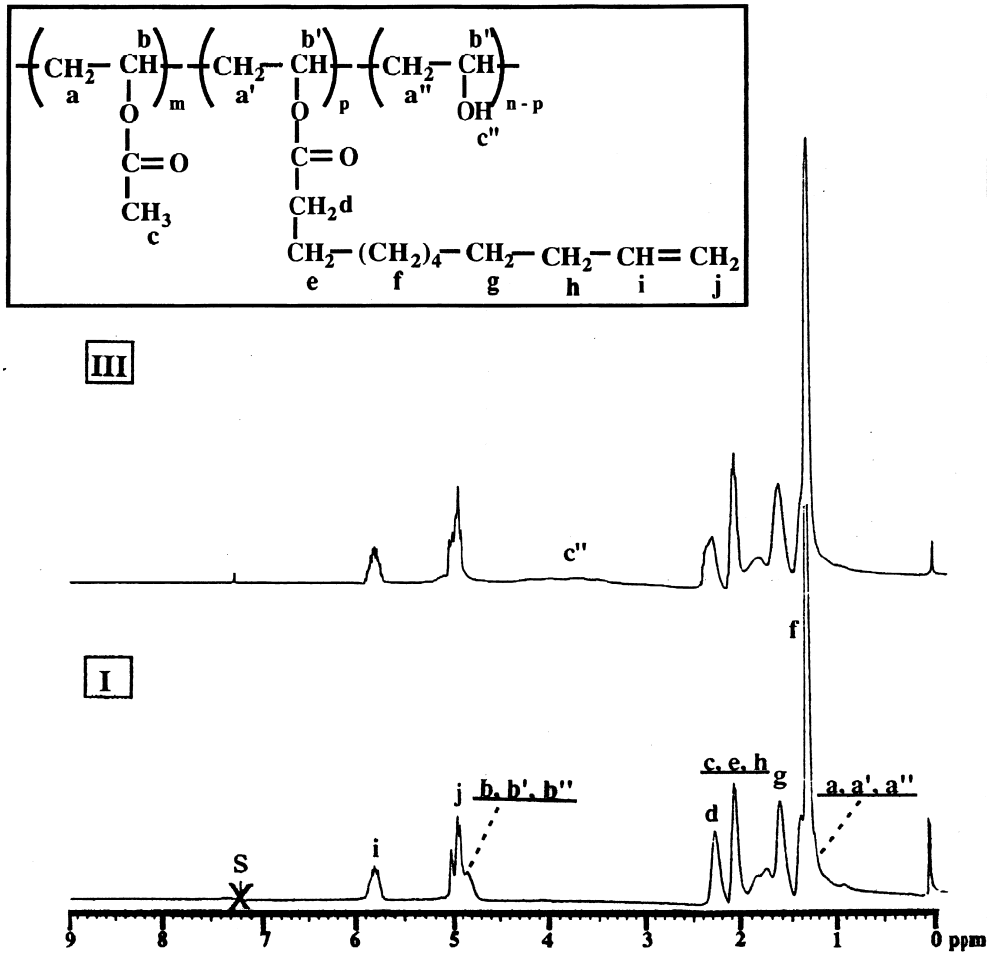

Fig. 1. ^{1}H-nmr spectra ($CDCl_3$) of vinyl alcohol-vinyl (10-undecenoate) copolymers (I) (80% 10-undecenoate groups) and (III) (39% 10-undecenoate groups).

used, but increasing the amount of acid chloride did not increase the degree of esterification very much. Likewise, the use of temperatures higher than room temperature did not improve the results. Different reaction times were also tested (5 h, 8 h, 1 day, 2 day, 7 day) but a noteworthy increase in esterification was only observed at first, and a maximum modification was reached at 1–2 days. Longer times did not improve the degree of esterification. This suggests that a plateau (80–85%) is reached at room temperature and a 2-day reaction. In addition, the esterification was also carried out by an interfacial reaction of the polymer with the acid chloride. This involved applying the Schotten–Baumann process, used succesfully in previous works [6–8] with acid chlorides which are more resistant to hydrolysis, but in this case the results were not satisfactory or reproducible because the 10-undecenoic acid chloride is prone to hydrolize and this reaction is faster than esterification.

Thus, the above preset reaction conditions and different ratios (OH/acyl chloride) were used in order to obtain several degrees of modification. Table 1 summarizes these results and some characteristics of the modified polymers. To estimate the weight average molecular weight of starting PVA, the corresponding poly(vinyl acetate) was synthesized [9] and the resulting polymer was characterizated by SEC–MALLS. Thus, from the $\bar{M}_w$ of starting PVA and the degree of modification, $\bar{M}_w$ estimated was calculated. The experimental $\bar{M}_w$ of the modified polymer was determined by SEC–MALLS and in all cases $\bar{M}_w$ was higher than the $\bar{M}_w$ estimated. The $\bar{M}_w/\bar{M}_w$ estimated ratios suggested that crosslinking side reactions took place to a certain extent.

The IR spectra (film on KBr) showed absorptions (cm^{-1}) at 3450 (OH), 3070 ($=CH_2$), 1737 (C = O), 1640 (C = C) and 906 (= CH) which confirm that esterification had taken place, albeit only partial in the three cases.

Fig. 1 shows the ^{1}H-nmr spectra of I (80% 10-undecenoate groups) and III (39% 10-undecenoate groups), but only slight differences can be seen related to the difference in 10-undecenoate group content. Signals corresponding to the aliphatic protons of the side chain appear between 1.1–2.4 ppm overlapped with the methylene protons of the main chain and the methyl of acetate groups [10] Around 4.8 and 5.9 ppm olephinic protons of the 10-undecenoate groups appear. Taking into account that the methine protons split and shift downfield, in comparison with the unmodified PVA when esterification occurs [11–13] it

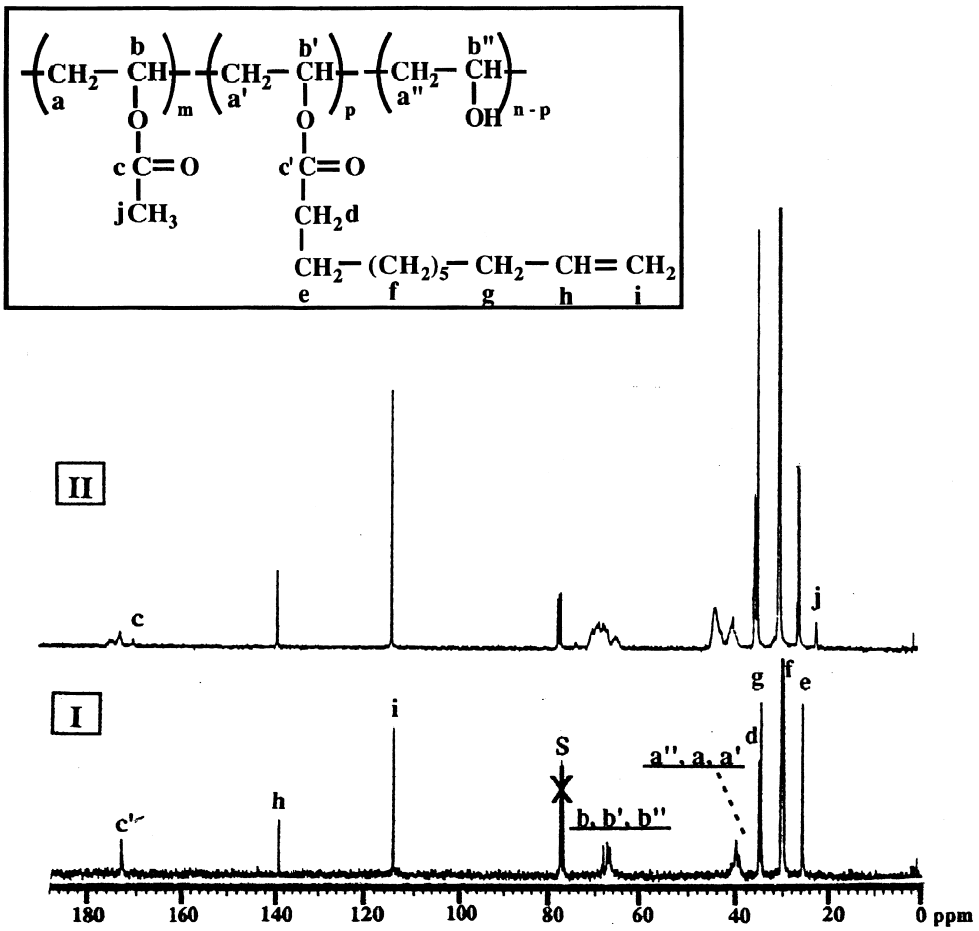

Fig. 2. ^{13}C-nmr spectra ($CDCl_3$) of vinyl alcohol-vinyl (10-undecenoate) copolymers (I) (80% 10-undecenoate groups) and (II) (55% 10-undecenoate groups).

seems probable that the esterified methine proton signal overlaps with the double bond proton signal around 4.8 ppm. The hydroxyl protons of unmodified PVA, which appear between 4.0 and 5.0 ppm when the spectrum is recorded in DMSO-d_6 [14,15], give no considerable signals in $CDCl_3$, although a broad and weak curvature on the baseline can be observed in that zone for the copolymer with the highest hydroxyl group content.

This esterification can be also observed in the ^{13}C-nmr spectra. Thus, in Fig. 2 the spectra of copolymers I (80% 10-undecenoate groups) and II (55% 10-undecenoate groups) show that not only the signals attributable to the side chain (very similar for both copolymers) did appear but so did two different groups of signals around 40 and 70 ppm. These groups of signals correspond respectively to the methylene and methine carbons of the main chain, with the expected variations [16,17], methylene upfield and methine downfield, according to the degree of modification. Differences can also be observed in the carbonyl zone where the signal of the initial acetate group and the new ester group should appear. The acetate carbonyl group, however, does not appear when the degree of esterification is very high.

The TGA plots of the three synthesized copolymers (Fig. 3) show that the degradation occurs at about 300°C, in two steps which should be attributable to the cleavage of the main chain and side chain. As can be seen in Table 2, the degree of substitution scarcely influences the temperatures of maximum rate of degradation of either step. DSC plots only showed the glass transition temperatures before degradation. As expected, the more long side chains introduced in the PVA, the lower the T_g value. Moreover, the more modified PVA shows a DSC exotherm due to a foreseeable thermal crosslinking of vinyl double bonds. However, the baseline did not recover since crosslinking and degradation overlap above 300°C.

These results seemed to suggest that initiators should be used to prevent degradation processes during the crosslinking and so obtain thermosetting materials. Dicumyl peroxide (5% w/w) was chosen as initiator, according to the results reported in a previous work about the modification of poly(epichlorohydrin) with the same side chain [18]. This initiator allows the polymerization of double bonds through a radical mechanism.

DSC is a valuable technique for investigating the curing reaction of crosslinkable polymers. Table 3 summarizes the DSC data of this crosslinking. An exotherm with a maximum below 200°C appeared, attributable to the decomposition of the initiator and the initiated polymerization of

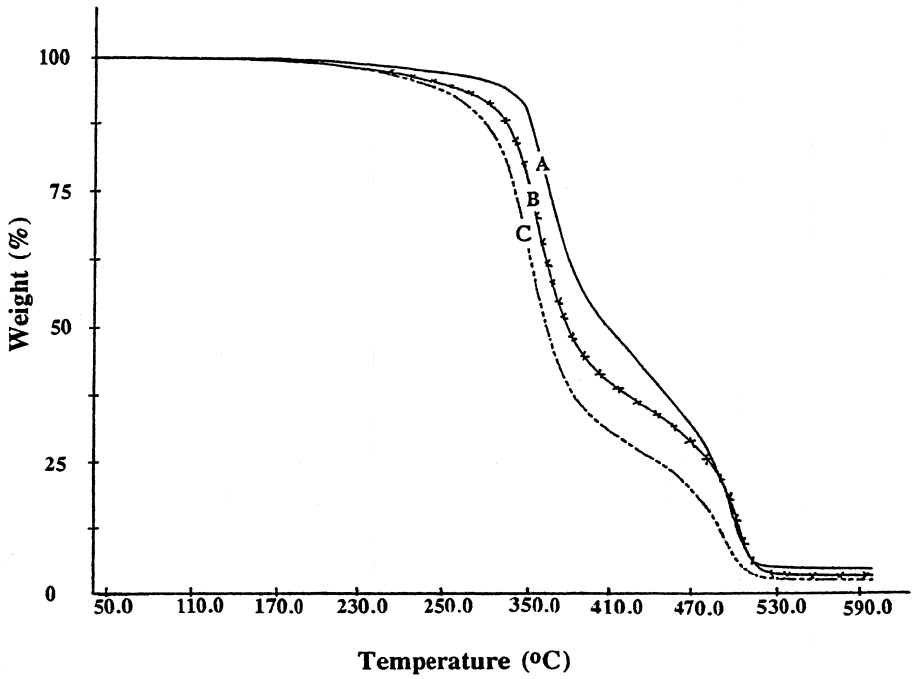

Fig. 3. TGA plots (20°C min^{-1}) of vinyl alcohol-vinyl 10-undecenoate copolymers: A, 80%; B, 55%; and C, 39% of 10-undecenoate groups.

double bonds. This maximum temperature shifted to lower values when the number of polymerizable sites is higher, suggesting an easier crosslinking. Dynamic DSC scans up to 250°C gave materials which were completely insoluble in all solvents tested. The T_g of the cured polymers was then determined by DSC and there was a considerable increase in T_g in all cases (Table 2), which was higher for the more modified polymers. It should be noted that in all cases the above-mentioned thermal crosslinking and degradation processes remain and can be detected above 300°C.

Thermogravimetric studies show that thermal stability increases when the curing takes place, and this increase is more significant when the degrees of modification are higher. Thus, as can be seen in Table 2, for copolymer I the temperatures of maximum rate of weight loss of both steps are higher and the weight loss is lower. Moreover, the residual weight at 600°C is higher for the peroxide-initiated cured materials than for those that were thermally crosslinked.

Isothermal and dynamic studies [19] are among the methods used to extract kinetic information from DSC curves. The isothermal method allows the reaction order and activation energy to be determined by performing a series of isothermal scans at different temperatures.

A commonly used dynamic method is based on the fact that the exotherm peak temperature varies predictably with the heating rate. Simple relationships between activation

Table 2
Thermal characterization of vinyl alcohol-vinyl 10-undecenoate copolymers (I, II and III)

	Linear polymers			Crosslinked polymers		
	I	II	III	I	II	III
Double bond (%)[a]	80	55	39	—	—	—
T_g (°C)[b]	−45	−34	−21	40	26	22
T_s (°C)[c]	348	329	313	366	348	333
$T_{10\%}$ (°C)[c]	346	324	312	352	338	320
T_{max1} (°C)[c]	351	350	349	390	388	382
ΔW_1 (%)[c]	24	22	20	12	14	18
T_{max2} (°C)[c]	498	496	490	544	541	534
ΔW_2 (%)[c]	14	13	11	29	32	33
$Y_{600°C}$	12	10	5	49	33	21

[a]Introduced groups (relating to 100 structural units of copolymer).
[b]Obtained by DSC at 20°C min^{-1}.
[c]Obtained by TGA at 20°C min^{-1}. T_s, start degradation temperature; $T_{10\%}$, 10% loss weight temperature; T_{max1} and T_{max2}, temperatures of maximum rate of weight loss; ΔW_1 and ΔW_2, weight loss at T_{max1} and T_{max2}; $Y_{600°C}$, residuum at $T = 600$°C.

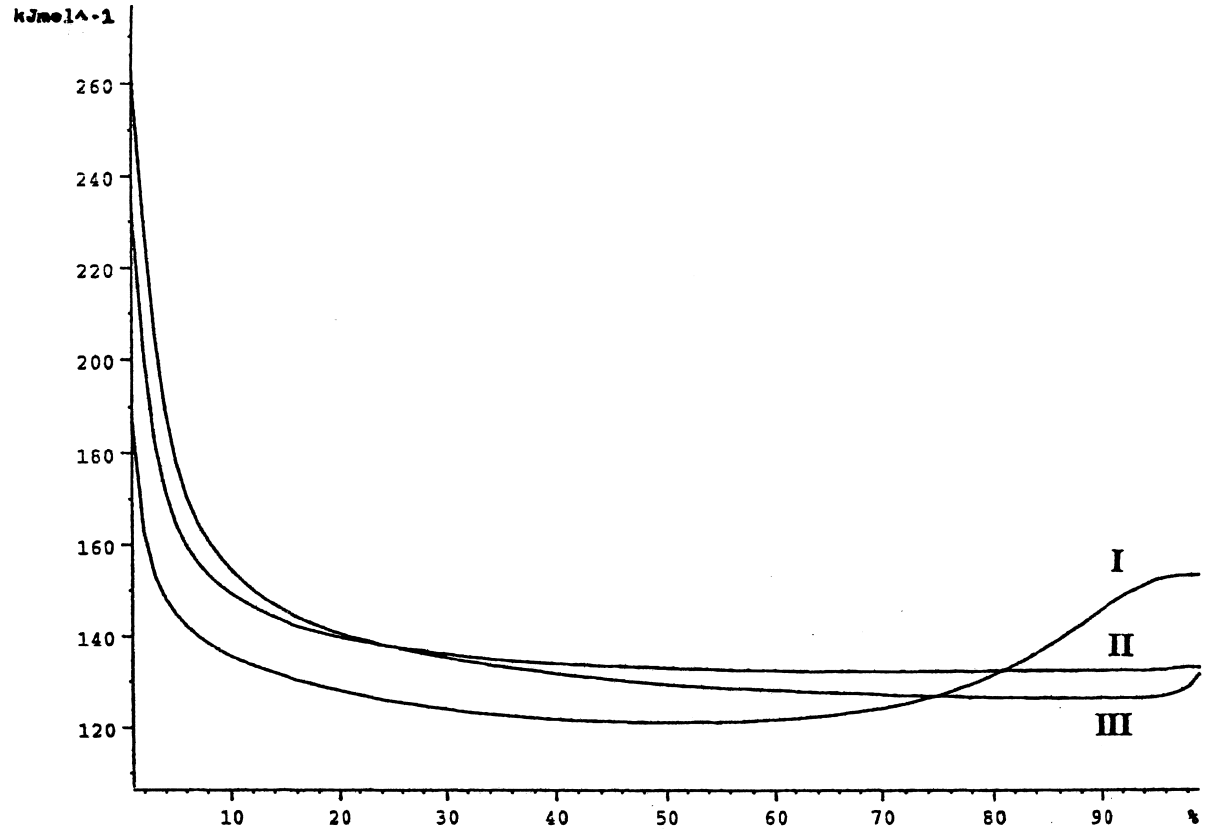

Fig. 4. E_a-conversion plots of dicumyl peroxide initiated crosslinking of vinyl alcohol-vinyl 10-undecenoate copolymers (I, 80%; II, 55%; and III, 39% of 10-undecenoate groups).

energy (E_a), heating rate (v) and exotherm peak temperature (T_p) have been deduced by Ozawa [20,21] $E_{a=} - R\,\Delta\ln v/1.052\,\Delta(1/T_p)$ and Kissinger [22]: $\ln(v/T_p^2) = \ln(AR/E_a) - E_a/RT_p$. This method has the advantage of allowing the activation energy to be calculated without previous knowledge of the reaction order.

In the present case, the isothermal method could not be used since the reaction rate was too high. This means that a considerable amount of heat evolved before the calorimeter was stabilized, and that the measurements obtained were unreliable. Thus, in this case, the use of the dynamic method was, in principle, recommended.

Table 3 also shows calculated activation energies for the initiated curing. The considerable concordance between the values obtained by the Ozawa and Kissinger expressions suggests a reaction order close to 1, since the Kissinger expression was strictly deduced for $n = 1$. As can be seen, the activation energies for the initiated processes increase as the degree of modification decreases, which suggests that crosslinking is more difficult when the degree of

Table 3
DSC crosslinking of vinyl alcohol-vinyl 10-undecenoate copolymers using 5% of dicumyl peroxide as initiator[a]

	I	II	III
Double bond (%)	80	55	39
T^b_{max}	175	189	190
ΔH (J g^{-1})	360	169	140
E_a (kJ mol^{-1})[c]	94	120	132
E_a (kJ mol^{-1})[d]	94	119	131
A (min^{-1})[e]	8.2×10^{11}	9.9×10^{11}	11.1×10^{11}

[a]Performed at 20°C min^{-1}.
[b]Maximum temperature of the exotherm of the initiated crosslinking process.
[c]Determined by using the Ozawa equation.
[d]Determined by using the Kissinger equation.
[e]Pre-exponential factor determined by using the Kissinger equation.

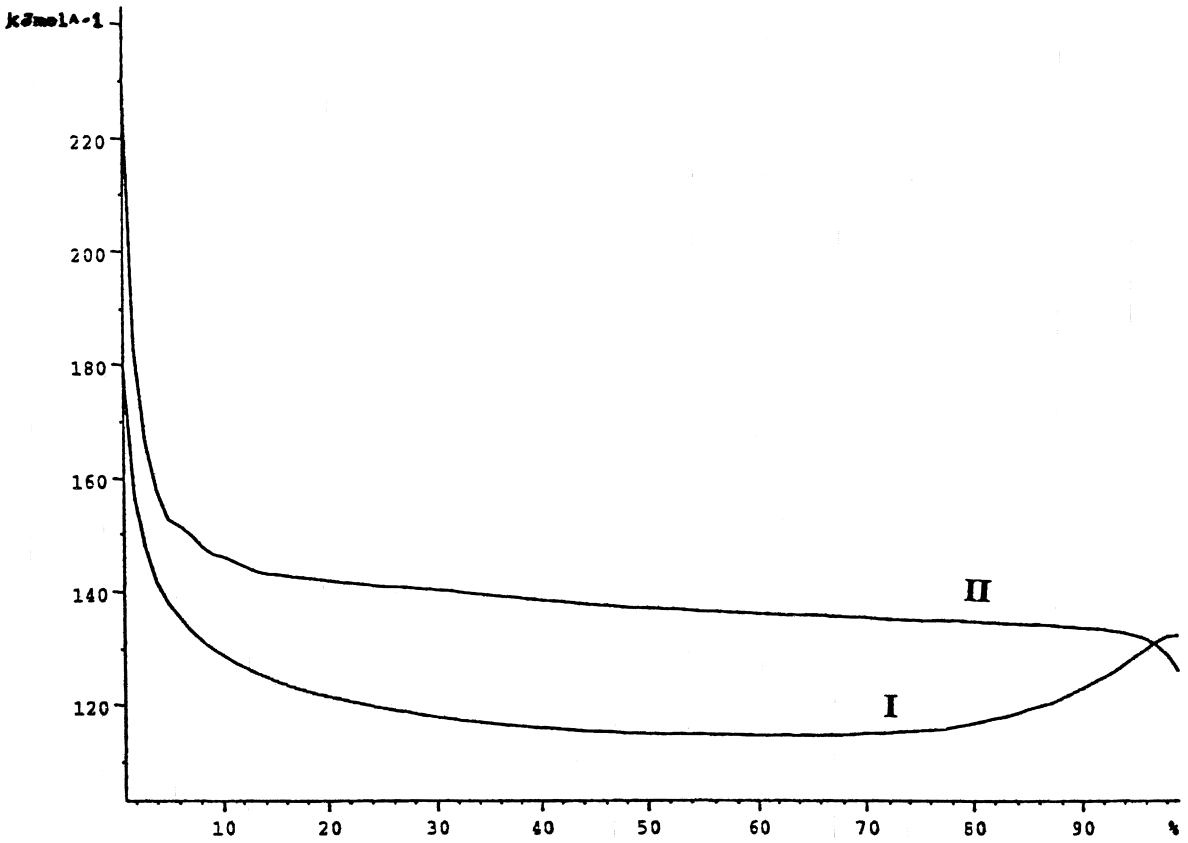

Fig. 5. E_a-conversion plots of dicumyl peroxide-initiated crosslinking of epichlorohydrin-glicidyl 10-undecenoate copolymers (I: 90%; and II: 50% of 10-undecenoate groups).

modification is lower, probably due to the fewer possibilities of collision among reactive sites.

As is evident, this curing process involves several reactions, namely initiation, propagation, termination and chain transfer, and therefore the isoconversional method is recommended [23]. Thus, Arrhenius parameters (E_a and A) should be considered as effective values, that can vary with changing temperature and conversion. The shape of this dependence is conditioned by the change in the contributions of different steps to the overall rate during the process. The change in these contributions depends on the process mechanism. Therefore, by analyzing the conversion dependence of the effective activation energy of the process, it is possible to understand the process kinetics without knowing the real rates of the reaction steps. Isoconversional kinetic analysis is based on the idea that the reaction rate at a constant conversion depends only on the temperature. For a single step process, E_a is independent of the degree of conversion and may have the meaning of the intrinsic activation energy. Multistep processes reveal that E_a depends on the degree of conversion, the analysis of which helps not only to reveal the complexity of a process, but also to identify its kinetic scheme.

Fig. 4 shows the plot of E_a vs conversion for the initiated crosslinking of the three polymers synthesized. As can be seen, the dependence of E_a on conversion has a sharply decreasing shape at the beginning of the reaction and reaches an almost constant value at about 10–15% of conversion. The initial high E_a values may mainly be associated to the initiator decomposition and the initiation step. When the contribution of the propagation step in the overall rate of reaction is predominant the constant value is reached. For polymer I (80% of 10-undecenoate groups), an increase in the activation energy can be observed from 70% of conversion, which may be due to the loss in mobility of the growing chains because of the high crosslinking degree reached as a consequence of the high degree of modification.

To test the influence that the polymeric main chain may have on the crosslinking of these 10-undecenoate pendant chains, the isoconversional kinetic method was also applied to two analogous polymers derived from poly(epichlorohydrin) with a comparable degree of modification (50% and 90%) and synthesized as reported [24]. The E_a-conversion curves shown in Fig. 5 behave in a similar fashion which suggests that the crosslinking mechanism must be the same and that the influence of the main chain is practically negligible. For the 90% substituted polymer the E_a increase occurs at slightly higher conversion values, which may be attributed to the higher mobility of the network due to the greater flexibility of the polyether main chain.

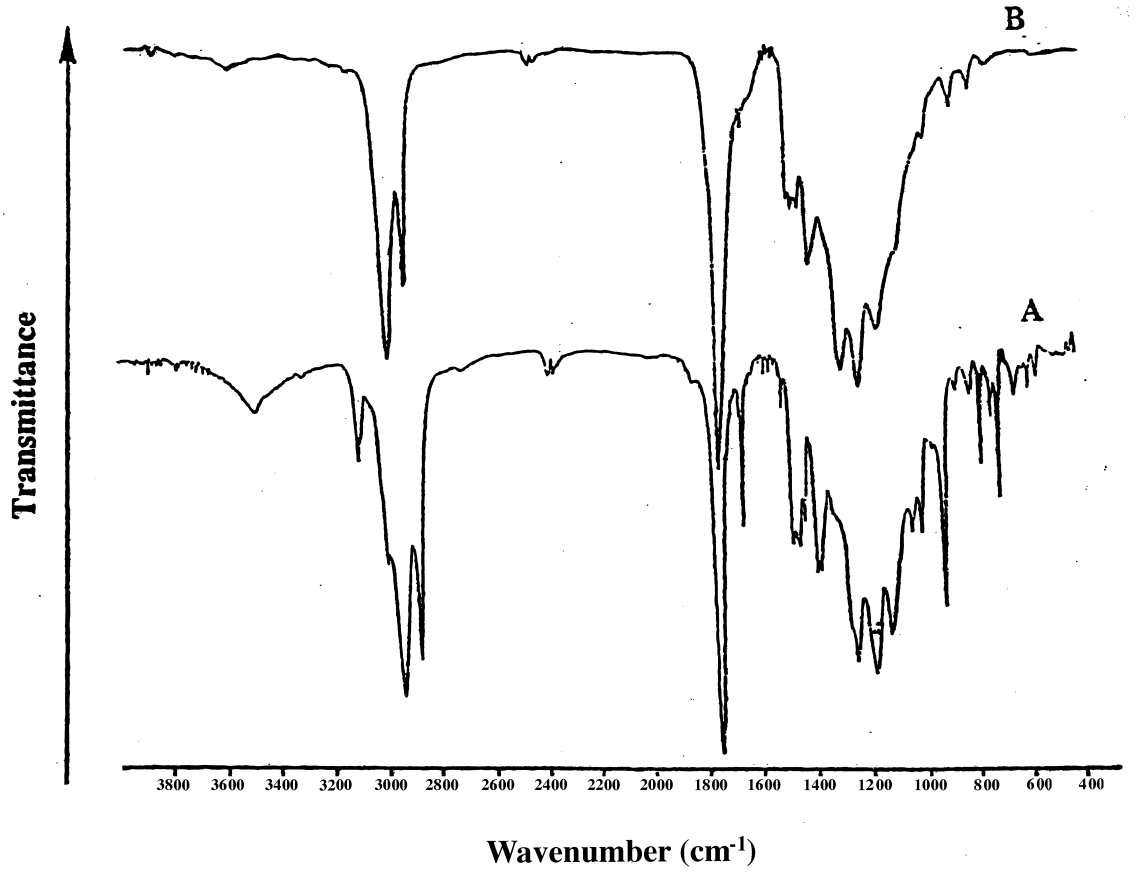

Fig. 6. IR spectra of a mixture of vinyl alcohol-vinyl 10-undecenoate copolymer (80% 10-undecenoate groups) and 5% of dycumil peroxide before (A) and after 1 h curing process (B).

To monitor the curing by IR spectroscopy, films of the polymers with the initiator were made on KBr pellets. These films were heated on air for 1 h at 150°C and the IR spectra recorded at different times. After this heating (spectrum B), the intensity of the double bond peaks (3070, 1640 and 906 cm^{-1}) decreased considerably, as can be seen in Fig. 6 for the highly modified polymer I (spectrum A).

By measuring the decrease in the areas of C = C stretching bands (1640 cm^{-1}) in relation to the unchanged area of the carbonyl group, the crosslinking process was monitored

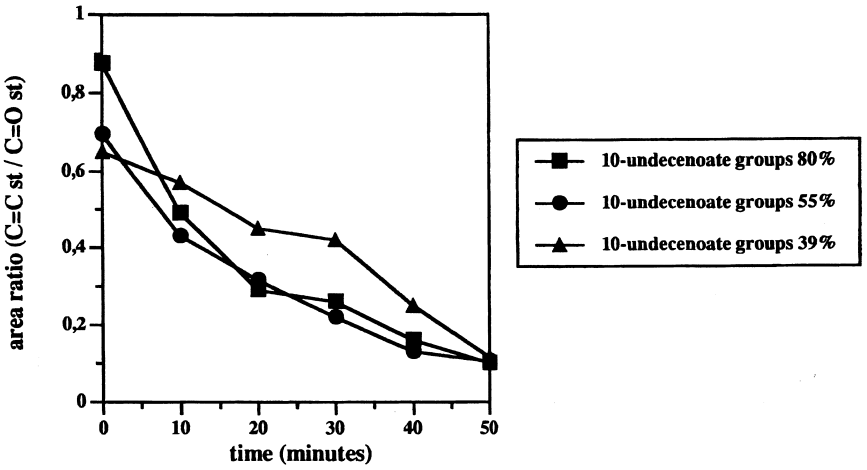

Fig. 7. Decrease in the amount of double bonds vs time.

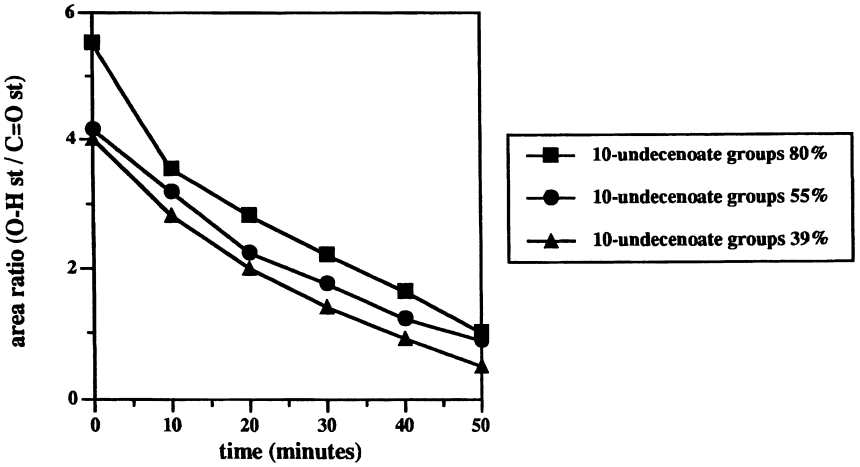

Fig. 8. Decrease in the amount of hydroxl groups vs time.

as is shown in Fig. 7. Moreover, a decrease in the OH stretching signal was also observed during this process as can be seen in Fig. 8. This is in agreement with the described dehydration that PVA undergoes when it is heated above about 120°C, leading to double bonds [25]. The low content in hydroxylic groups in the crosslinked polymer should be the reason for the low water uptake which in no case reached 20%.

Acknowledgements

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