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Synthesis of Butadiene-Acroleine Block Polymers
Cross-Link Under UV Cure

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SUMMARY.

From GPC and ^{1}H NMR results, we have shown that block polymers built with acroleine and butadiene units can be synthesized. Moreover, the cross-linkage ability of the acroleine blocks in these products under UV irradiation has been checked. This is very interesting for an industrial application. Indeed, homopolyacroleines can be used as a photopolymer layer to prepare negative or positive printing plates.

INTRODUCTION.

Previously, using ^{1}H and ^{13}C NMR, anionic polyacroleines have been shown to contain several types of units : (1,2), (1,4) , (3,4) (GULINO et al. 1981 a). The results of the microstructures show (1,2) units are mainly synthesized at the beginning of polymerizations. In tetrahydrofuran, the (1,2) percentage decreases as the molecular weight increases and becomes constant around 12 %. To explain the formation of the different units and the heterogeneity in the microstructure, the propagation mechanism must involve two different types of living end (GULINO et al. 1981 a). Moreover, the anionic polymerization involves numerous transfer reactions to the monomer and to the polymer (GULINO et al. 1979). These reactions induce a considerable increase in the polydispersity index of the molecular weight distributions. Nevertheless, in spite of these secondary reactions, it is possible to synthesize butadiene - acroleine block polymers. Butadiene is the first monomer to be polymerized. Then the butadienyl living ends are used for initiating small amounts of acroleine. In fact, copolymers with short acroleine blocks can be obtained and in these conditions, the formation of homopolyacroleines can be avoided. It would be better to speak about functionalization rather than block polymer syntheses. The syntheses of the butadiene - acroleine block polymers can be controlled by GPC (GULINO et al. 1981 b). For example, Fig. 1 shows the GPC chromatograms of a butadiene initiator and that of the corresponding block polymer. A bimodal distribution can be seen simultaneously on the RI and UV responses. A simultaneous shift of the two distributions above the molecular weight of the initiator can be noticed. All the living ends of polybutadiene initiate the acroleine polymerization

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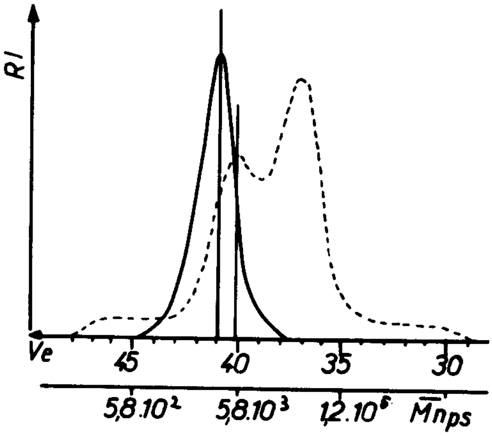


Figure 1

Acroleine initiation by an α-ω disodium oligobutadiene in THF at - 40°C

(——) : initiator ; $\overline{M_n}$ = 1 600

(- - - -) : PAB_{10} after the acroleine polymerization

Figure 2

Modification of IR spectra by UV cure (λ = 3 500 Å)

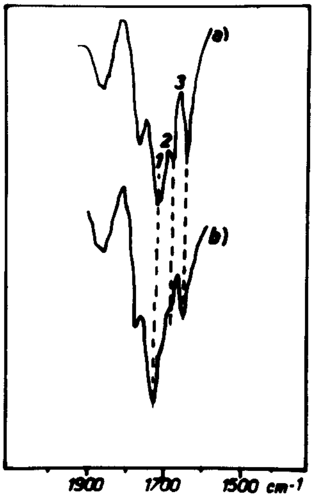
a) polyacroleine before irradiation

b) the same polyacroleine after irradiation

(1) : $\lambda > C = O$: (1,2) unit (1720 cm^{-1})

(2) : $\lambda > C = C <$: (1,4) unit (1680 cm^{-1})

(3) $\lambda > C = C <$: (3,4) unit (1650 cm^{-1})



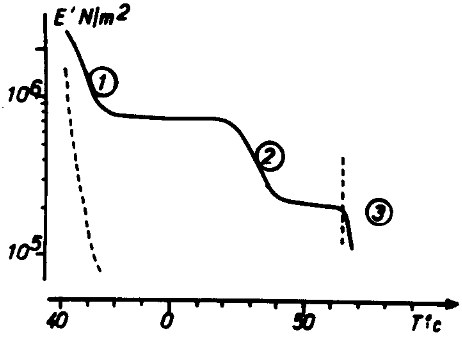


Figure 3

Evolution of E' for PAB_{14} at 31 Hz

(- - - -) oligobutadiene

(——) PAB_{14} block polymer

(1) : relaxation of butadiene blocks

(2) : relaxation of acroleine blocks

(3) : degradation of acroleine blocks

and lead to two different types of macromolecules : Indeed, some copolymer chains contain long acrolein blocks while others are constituted with only two or three acroleine units.

Moreover, several authors (G. MANECKE et R. POHL 1976 ; R.C. SCHULZ et al. 1967) have modified polyacroleines chemically for some industrial utilizations, characterising the structure of the polymers imperfectly.

The purpose of this article is to check the cross-linkage ability (under UV cure) of anionic homopolyacroleines and butadiene acroleine block polymers.

EXPERIMENTAL.

The homopolyacroleines and the block polymers built with acroleine and butadiene units are initiated by lithium or sodium naphthalene complexes in tetrahydrofuran.

The mechanical behaviour of the block polymers has been studied on a Metravib apparatus. On this instrument, it can be directly displayed the complex stiffness and the loss angle between stress and strain, for some frequencies ranging from 7,8 to 1000 Hz at different temperatures varying from - 40°C up to + 200°C.

RESULTS AND DISCUSSION.

We try to determine the nature of the monomeric units which can crosslink under UV cure in polyacroleine chains. The IR spectroscopy is a very well adapted method to follow qualitatively modifications due to the photochemical reactions. Several KBr pellets which contain polyacroleines have been directly insolated. After the irradiation, the IR spectra show :

- A decrease in the $> C = C <$ absorptions at 1650 cm^{-1} (3,4 units) and also at 1680 cm^{-1} (1,4 unit). Indeed, the (1,4) units disappear more quickly than the (3,4) units.
- At the same time, an increase of the $> C = O$ absorption (at 1720 cm^{-1}) can be noticed (Fig. 2). These observations support that during an UV irradiation a crosslink of the $> C = C <$ double bond occurs. But also some photodegradation takes place with formation of $> C = O$ bond.

The evolution of the mechanical behaviour has been also studied to test the cross-linkage ability of the butadiene - acroleine block polymers. This method has been applied to a copolymer which has been photocured during four minutes without photosensitizer $\lambda > 3\ 000$ Å. (This copolymer contains 37 % of acroleine units and the microstructure of the acroleine block is % $\underline{(1,2)}$ = 60 ; (3,4) + % (1,4) = 40. The polybutadiene block has a $\overline{M_n}$ = 7000).

The figure 3 shows the variations of the storage modulus (E') at 31 Hz and in a temperature ranging from - 40°C to + 90°C.

Two kinds of relaxations can be noticed. This seems logical because two types of blocks exist in this copolymer. The decrease of E' around T = - 35°C can be attributed to polybutadiene blocks. Indeed, it is known that a polybutadiene having a molecular weight of 700 and which contains 18 % (1,4) units possesses a glass transition around - 40°C. Likewise , the relaxation which begins at + 20°C can be allotted to acroleine blocks.

On the other hand, the drop in the modulus over 65°C corresponds to the destruction of the acroleine blocks.(The same phenomenon can be noticed with the homopolyacroleines around 70°C). In comparison, the chains of polybutadiene have neither chemical nor physical cross-links and consequently no rubbery zone. On the other hand, after an UV cure, the block polymer presents a rubbery zone belonging to polybutadiene blocks. Some chemical cross-links have been created and can be explained by the formation of a polyacroleine network. The acroleine units can cross-link under UV cure as well in the block polymers as in the homopolyacroleines. So it may be possible to obtain a printing plate using homopolyacroleines or block polymers as a photopolymer layer. The most interesting attempt has been obtained from a polyacroleine synthesized in THF with Na^+ as a counter ion at - 30°C : the polymer solution, to which β methyl anthraquinone (used as a photosensitizer) is added at the end of the anionic synthesis, has been directly poured onto an aluminium plate. Then, after drying, the printing plate covered with a thick polyacroleine film (1 - 2 μ) has been insolated during four minutes under an UV lamp (λ > 3 000 Å) through a photographic negative. The exposed areas become insoluble and adhere to the metallic plate. On the other hand, the unexposed parts are taken off using ethoxy ethylacetate. So after a water rinsing, the cross- linking polyacroleines provide ink receptive areas. This attempt is very interesting because of the sharpness of the printing image. So, homopolyacroleines and block copolymers could be used as photopolymer layers to prepare negative printing plates. Moreover, the ability of these polymers to degradation around 70°C makes them useful as positive printing plate, as well.

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