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Polymeric surface coatings for use as leather finishes—Part I. Studies on synthesis and characterisation of urethane acrylate oligomers

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Abstract. Synthesis and characterisation by NMR spectroscopy of oligomers derived from 2-hydroxy ethyl acrylate (HEA) and 2-hydroxy propyl methacrylate (HPMA) and 1,6-hexamethylene diisocyanate (HDI) are briefly discussed.

Keywords. Surface coating; oligomers; thermosetting acrylics.

1. Introduction

Oligomers afford a convenient means of incorporating diverse characteristics into the cross-linking systems and as such are extremely useful. Thermosetting acrylics are a recent class of coatings (Hutchinson 1971 ; Kubena Jiri 1973) and the basic principle underlying the synthesis of this kind of acrylics involve the incorporation of reactive monomers or oligomers (Maslyuk 1973 ; Myers and Long 1976 ; Spirin *et al* 1972) of cross-linking type into the system. Thermosetting acrylics find a variety of special applications (Anon 1974, 1975, 1976) and the present study aims at developing suitable oligomers for use in the thermosetting systems so as to develop suitable coating composition for the leather industry. The reactive monomers and resin co-reactants used in the cross-linking reactions for thermosetting acrylic polymer are given in table 1.

The present study reports the synthesis of two oligomers from 2-hydroxy ethyl acrylate and hexa methylene diisocyanate and from 2-hydroxy propyl methacrylate and hexamethylene diisocyanate. The oligomers are then subjected to NMR spectroscopy for the structural elucidation. Only a few reports are available on this kind of systems (Okamoto *et al* 1975 ; Reinhardt Heiny 1970) and it has therefore been considered worthwhile to study the synthesis of the above oligomers.

2. Experimental

2.1. *Materials*

(i) 2-hydroxy ethyl acrylate (HEA) (Fluka-A.G.) ; (ii) 2-hydroxy propyl methacrylate (HPMA) (Fluka) ; (iii) Hexamethylene diisocyanate (HDI) (Fluka) ; (iv) Dibutyl tin-dilaurate (Veba-chimie).

Table 1. Cross-inking reactions for the thermosetting acrylic polymers.

Pendant group on acrylic polymer backbone	Reactive monomer containing pendant group	Resin co-reacted to effect cure
$-CONHCH_2OR$	Acrylamide or methacrylamide converted with formaldehyde and alcohol to an ether	Epoxy melamine formaldehyde urea formaldehyde
$-CH_2OH$	Hydroxy ethyl or propyl acrylate/ methacrylate	Melamine formaldehyde–urea formaldehyde
$-COOH$	Acrylic or methacrylic acid	Epoxy
$-\overbrace{CH-CH_2}^{O}-$	Glycidyl methacrylate	Methacrylic acid, acrylic acid

2·2. *Methods*

The hydroxy acrylate monomers have been purified by distillation under reduced pressure and stored at low temperature. The diisocyanate and the catalyst dibutyl tin-dilaurate were used without further purification. The purity of the diisocyanate estimated according to standard method (Saunders and Frisch 1973) was of the order of 99·5%. The oligomers were synthesised by adopting the following procedure.

To a clean two-necked flask, well cooled by icebath and fitted with stirrer, nitrogen inlet and dropping funnel hexamethylene diisocyanate (84·1 g) was added and nitrogen bubbled for 10 min. To this 2-hydroxy ethyl acrylate (115 g) containing dibutyl tin-dilaurate (2 drops, *i.e.*, 0·001% on the weight of monomer) was added gradually with stirring for 30 min. The reaction flask was left for another 30 min and the oligomer which was of semi-solid consistency was removed and stored under nitrogen at low temperature. The above procedure was repeated for the oligomer synthesis involving 2-hydroxy propyl methacrylate (144·1 g) and hexamethylene diisocyanate (84·1 g) to yield a waxy solid which was then stored under nitrogen at low temperature.

These two oligomers were then subjected to NMR analysis by dissolving in CCl_4 and using the NMR spectrophotometer (Varian T-60). TMS was used as reference. The spectra recorded are shown in figures 1 and 2 along with the delta values assigned for the proton shift.

3. Results and discussion

The synthesis of oligomer affords a convenient means of introducing urethane linkage into the structure which could subsequently be incorporated into the thermosetting composition. Our main objective has been to ascertain the nature of oligomer formed and as such the main attention was devoted to finding the structural characteristic through NMR analysis. Therefore the results of

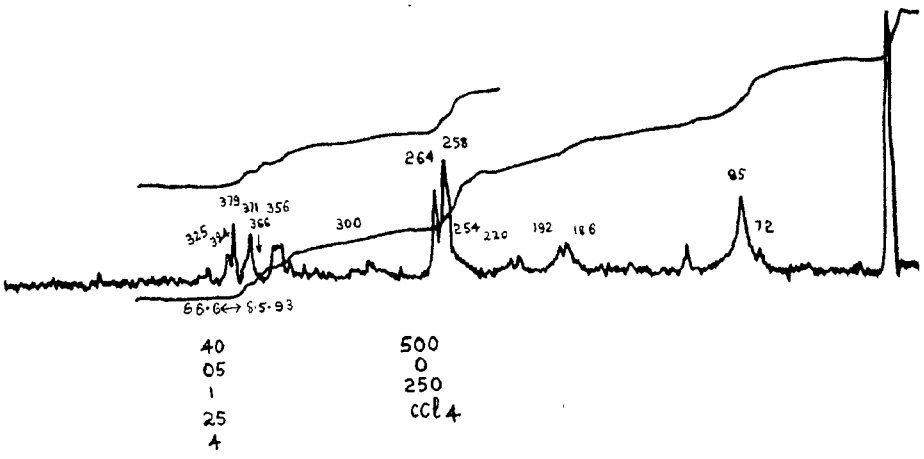


Figure 1. NMR spectrum for 2-hydroxy ethyl acrylate hexamethylene diisocyanate oligomer.

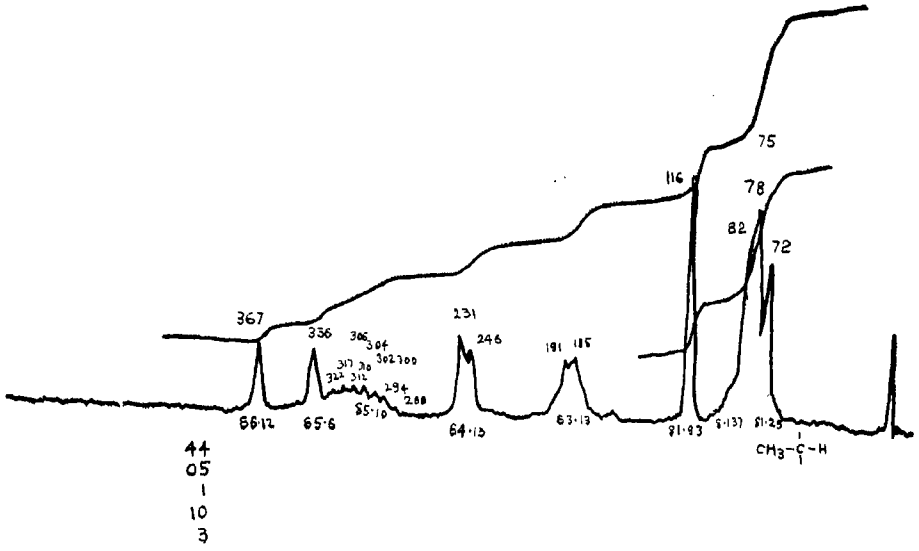
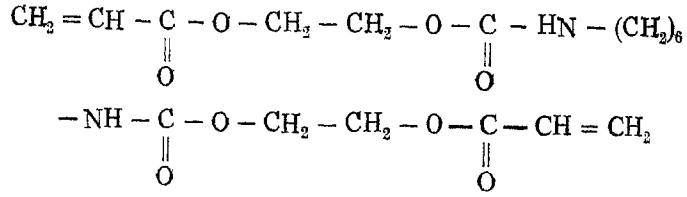


Figure 2. NMR spectrum for 2-hydroxy propyl methacrylate hexamethylene diisocyanate oligomer.

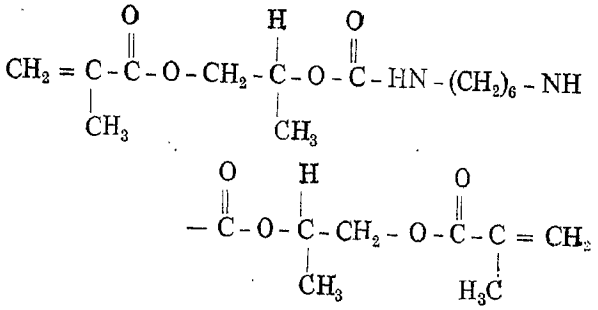
NMR are described in terms of delta values and the structure assigned on the basis of this evidence. The assigned structure confirm the formation of the desired oligomer with its acrylic double-bond in tact. This has been further corroborated in other similar experiments (to be published).

The hexamethylene diisocyanate and 2-hydroxy ethyl acrylate oligomer indicated the following results on the NMR spectrum (figure 1). For assigning delta values the protons have been grouped under 4 sets : (i) Vinyl hydrogens are present as a six-proton multiplet at delta values in the range of 5·96 to 6·61 in the spectrum. This signal is characteristic of the vinyl group protons as observed with methylacrylate. (ii) Ethylene protons appeared at delta values 4·35 as

unresolved doublets. (iii) At delta value 3·4 the presence of four proton multiplet is assigned to the two CH_2 attached to N atom. (iv) The four CH_2 group protons are represented by a broad singlet at delta value 1·41. The two NH group hydrogens are present as broad band for 2 protons. These data give rise to the structural representation reproduced below :



The NMR spectrum for oligomer from hexamethylene diisocyanate and hydroxy propyl methacrylate gave the following results. In terms of the delta values assigned (figure 2) (i) the two pairs of poorly resolved doublets occurring at delta values 5·6 and 6·12 can be ascribed to the terminal two CH_2 protons. The resolution is, however, not sharp due to different plane of symmetry. (ii) The four methylene hydrogens attached to carbon bonded to oxygen appear as a pair of doublets at delta value 4·13 and the two CH_2 protons bonded to nitrogen as a multiplet at delta value 3·13 in the spectrum. (iii) The spectrum indicates a 6-proton singlet at delta value 1·93 attributable to two methyl groups attached to the double bond carbon and the downward shift occurring indicates that these may be due to conjugation of the double bond with carbonyl group. (iv) The 6-proton doublet at delta value 1·25 shows that two methyl groups in the structure present as CH_3-C-H. (v) A broad multiplet is present at delta value 5·10. This has been due to protons on the carbon attached to CH_2 as well as CH_2 groups. This also overlaps the signal from N atom. (vi) The hydrogens from CH_2 groups appear as broad singlet at delta value 1·37. On the basis of the above observation the following structure has been assigned.



The present method therefore seems to be satisfactory as the formation of oligomers are in the right direction as indicated by the NMR spectra.

4. Conclusion

Oligomers are an interesting class of substances and the present study of synthesis and characterisation of urethane-acrylate oligomer affords the desired route to the thermosetting acrylics.

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