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SYNTHESIS, CHARACTERIZATION AND EVALUATION OF ALKYL 2-BROMOACRYLATES AS ADHESIVES

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Abstract—Various alkyl 2-bromoacrylates were synthesized in high purity and yield. They were characterized by spectroscopic techniques. The monomers were then formulated into aerobic adhesive compositions and their adhesive bond strengths between various surfaces were evaluated.

1. INTRODUCTION

The most common alkyl 2-bromoacrylates are the methyl, ethyl and butyl compounds [1, 2]. They are useful in the synthesis of graft polymers, by treating them with halosilanes [3]. They are also useful in organic synthesis and in bactericidal and fungicidal compositions [4–6], but no work has yet been reported on their use in adhesive formulations. In this communication, syntheses of some alkyl 2-bromoacrylates are reported along with their spectral characterization. Aerobic adhesive compositions based on these monomers and their bond strengths between various metal surfaces are reported.

2. EXPERIMENTAL PROCEDURES

2.1. *Synthesis of 2-bromoacrylates*

Synthesis of a 2-bromoacrylate consists of the sequence of reactions as shown in Scheme 1.

2.1.1. Synthesis of alkyl acrylates (1). Alkyl acrylates were prepared by reacting an alcohol (0.25 mol) with acrylic acid (0.3 mol) in the presence of *p*-toluenesulphonic acid (PTSA) (1% of total reactants) and benzene in an amount equal to the total weight of reactants. The water of reaction was removed azeotropically using a Dean-Stark trap. After completion of the reaction, the reaction mixture was washed with water to remove excess acrylic acid and dried with anhydrous Na_2SO_4; the solvent was removed and the product was distilled under reduced pressure.

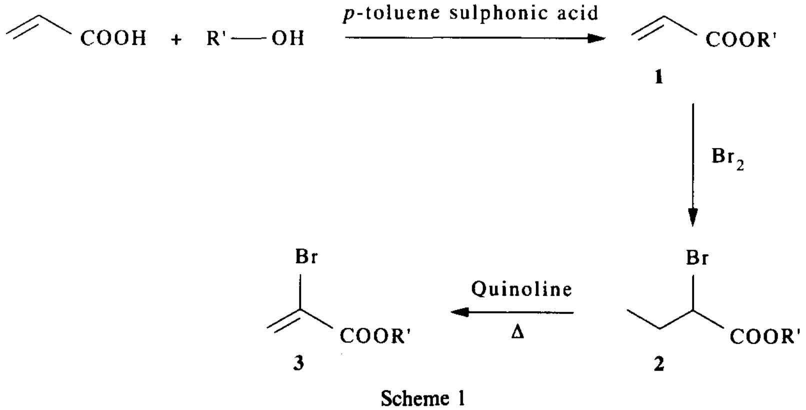
2.1.2. Synthesis of alkyl 2,3-dibromopropionates (2). Alkyl acrylate (0.15 mol) was placed in a flask fitted with a stirrer, thermometer and dropping funnel. Chloroform (10 ml) was added, and the flask was immersed in an ice bath. Bromine (0.17 mol) was added slowly to the reaction mixture over a period of 3–4 hr, while the temperature was maintained below 40°. After completion of the reaction, $CHCl_3$ was removed and the product was purified by vacuum distillation. The physical properties of various alkyl 2,3-dibromopropionates are reported in Table 1.

2.1.3. Synthesis of alkyl 2-bromoacrylates (3). Alkyl 2-bromoacrylates were prepared by heating alkyl 2,3-dibromopropionate (0.04 mol) with quinoline (0.057 mol) at 100° for 30 min under N_2. The reaction mixture was then dissolved in $CHCl_3$ (50 ml) and this solution was washed thoroughly with 5% aqueous HCl to remove unreacted quinoline, and then with water to remove the mineral acid. The organic layer was separated and dried, and then the solvent was removed. The physical properties of various alkyl 2-bromoacrylates are reported in Table 2.

2.2. *Synthesis of bis(2-bromoacrylate)*

Diethyleneglycol bis(2-bromoacrylate) was prepared accordingly as shown in Scheme 2.

2.2.1. Synthesis of diethylene glycol diacrylate (4). Diethyleneglycol diacrylate was prepared by reacting diethylene glycol (53 g, 0.5 mol) with acrylic acid (86.4 g, 1.2 mol) in the presence of PTSA (1.0% of total reactants) as catalyst, and benzene (150 ml) as solvent. The water formed during the reaction was removed azeotropically



Scheme 1

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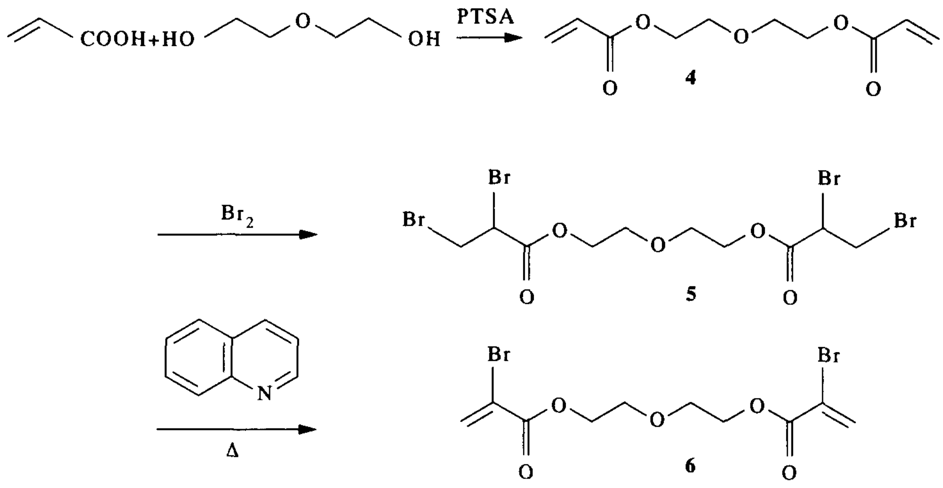


Scheme 2

through a Dean-Stark trap. After completion of reaction, the reaction mixture was washed and dried; the solvent was removed and the product was distilled under reduced pressure.

2.2.2. Synthesis of diethyleneglycol bis(2,3-dibromopropionate) (5). To diethyleneglycol diacrylate (18.9 g, 0.093 mol) and chloroform (20 ml), bromine (29.7 g, 0.186 mol) was added slowly. The product was purified by vacuum distillation, as described for the synthesis of alkyl 2,3-dibromopropionates (yield 85%, b.p. 200° at 2 mmHg, n_D^{38} 1.5320, d_4^{38} 1.9100).

2.2.3. Synthesis of diethyleneglycol bis(2-bromoacrylate) (6). Diethyleneglycol bis(2-bromoacrylate) was prepared by heating diethyleneglycol bis(2,3-dibromopropionate) (13.78 g, 0.026 mol) and quinoline (6.84 g, 0.053 mol) in $CHCl_3$ (20 ml) at 100° for about 1 hr under N_2, and then processed as described for 2-bromoacrylates (yield 75%, n_D^{38} 1.5128, d_4^{38} 1.6112).

2.3. Characterization of alkyl 2-bromoacrylates by spectroscopy

2.3.1. ^{1}H-NMR spectroscopy. In the ^{1}H-NMR spectra of alkyl 2,3-dibromopropionates, the two methylene protons adjacent to 'Br' ($Br—\underline{CH_2}—CHBr—COOR$) appeared as distorted triplet at δ 3.85–3.95 and double doublet (dd) at δ 3.60–3.70 and the proton on carbon attached to 'Br' and 'COOR' ($Br—CH_2—\underline{C}HBr—COOR$) appeared as 'dd' at δ 4.36–4.66 ppm. When alkyl 2,3-dibromopropionate was converted to alkyl 2-bromoacrylate, the above three peaks disappeared and two doublets at δ 6.87 and at δ 6.25 appeared for the two protons ($\underline{CH_2}{=}C(Br)—COOR$) as shown in Scheme 3.

In the ^{1}H-NMR spectra of alkyl 2-cyanoacrylates, the two terminal protons appeared at lower field than for alkyl 2-bromoacrylates, because of the greater electron-withdrawing nature of CN.

The chemical shifts of other protons in the alkyl group for all 2-bromo-acrylates prepared are reported in Table 3. The ^{1}H-NMR spectrum of 2-(1-methoxy propyl)bromoacrylate is shown in Fig. 1.

2.3.2. ^{13}C-NMR spectroscopy. The three characteristic peaks for the three carbons at 161.24 ($H_2C{=}C(Br)—\underline{C}OOR$), 130.34 ($\underline{C}H_2{=}C(Br)—COOR$), and 121.58 ($H_2C{=}\underline{C}(Br)COOR$) ppm appeared in the ^{13}C-NMR spectra of 2-bromoacrylates. The chemical shifts of other carbons are reported in Table 4.

The ^{13}C-NMR spectra of bromoethyl 2-bromoacrylate, and diethyleneglycol bis(2-bromoacrylate) are shown in Figs 2 and 3, respectively.

2.3.3. Mass spectroscopy. The most important diagnostic peaks for alkyl 2-bromoacrylates are shown in Scheme 4.

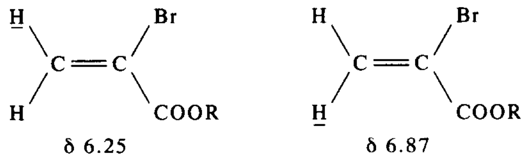
In alkyl 2-bromoacrylates, the base peak appeared at *m/z* 135, but in benzyl and 2-(1-methoxy propyl)bromoacrylates the base peak was R^+. Other important peaks are given below:

Methyl : *m/z*: 164, 166 (M^+), 84 ($M^+—HBr$)
Bromoethyl : *m/z*: 256, 258, 260 (M^+), 69 [($M^+—(R—HBr)$]
Benzyl : *m/z*: 240, 242 (M^+), 91 (Tropilium ion)
Cyclopentyl : *m/z*: 218, 220 (M^+), 138 ($M^+—HBr$), 69 ($C_5H_9^+$)
2-(1-methoxy propyl) : *m/z*: 222, 224 (M^+), 45 ($\overset{+}{C}H_2OCH_3$), [$\overset{+}{C}H(CH_3)CH_2OCH_3$], 142 [$M^+—HBr$], 177 ($M^+—CH_2OCH_3$).
Diethyleneglycol bis(2-bromoacrylate) : *m/z*: 177, 179 ($M^+—C_5H_6OBr$), 79, 81 ($\overset{+}{Br}$).

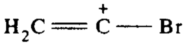
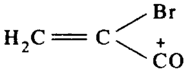
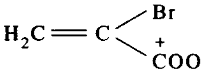
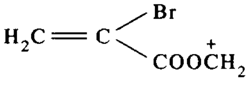
The mass spectrum of benzyl 2-bromoacrylate is shown in Fig. 4.

Table 1. Physical properties of the alkyl 2,3-dibromopropionates

Alkyl 2,3-dibromopropionates	Yield (%)	Boiling point °C (mmHg)	Density d_4^{38} (kg/m^3 × 10^3)	Surface tension at 38° (N/m × 10^3)	Refractive index n_D^{38}
Methyl	80	160–165 (25)	1.9167	40.10	1.5082
Bromoethyl	75	140–141 (8)	2.0730	48.00	1.5368
Benzyl	78	160–161 (7)	1.6527	41.50	1.5573
Methoxy 2-propyl	85	139–140 (15)	1.6200	38.50	1.4880
2,3-Dibromo propyl	83	160–161 (10)	2.2129	50.50	1.5643
Cyclopentyl	90	140–142 (7)	1.6518	41.20	1.5128
Acetoxy ethyl	88	180–181 (20)	1.6758	42.05	1.4839



Scheme 3

Fragment	m/z
 $H_2C{=}\overset{+}{C}{-}Br$	105, 107 (Isotopic peak)
 $H_2C{=}C(Br)\overset{+}{C}O$	133, 135 (Isotopic peak)
 $H_2C{=}C(Br)\overset{+}{C}OO$	149, 151 (Isotopic peak)
 $H_2C{=}C(Br)COO\overset{+}{C}H_2$	162, 164 (Isotopic peak)

Scheme 4

Table 2. Physical properties of the alkyl 2-bromoacrylates

Alkyl 2-bromo-acrylates	Yield (%)	Density d_4^{38} (kg/m³ × 10³)	Surface tension at 38° (N/m × 10³)	Refractive index n_D^{38}
Methyl	70	1.6614	28.10	1.4356
Bromoethyl	65	1.4794	28.00	1.5140
Benzyl	68	1.7058	29.15	1.5182
Methoxy 2-propyl	68	1.4592	26.10	1.4740
2-Bromoallyl	60	2.0216	35.50	1.4387
Cyclopentyl	80	1.5028	29.20	1.4523
Acetoxy ethyl	65	1.6102	30.21	1.4268

Table 3. ^{1}H-NMR (δ ppm) values of alkyl 2-bromoacrylates

Alkyl (R)	δ ppm values of alkyl protons
Methyl	3.81 (s, 3H)
Bromethyl	3.47–3.62 (t, 2H, 6), 4.53–4.56 (t, 2H, 6.5)
Benzyl	5.21 (s, 2H), 7.37 (s, 5H)
Methoxy 2-propyl	1.18–1.27 (d, 3H, 6.25), 3.35 (s, 3H) 3.43 (d, 2H, 7.5), 4.93–5.25 (m, 1H, 6)
Cyclopentyl	1.82–1.85 (m, 8H, 6.1), 5.18–5.26 (m, 1H, 6)
Acetoxy ethyl	2.12 (s, 3H), 3.62–4.37 (m, 4H, 6.2)
	Bis (2-bromoacrylate)
Diethyleneglycol	3.66–3.78 (t, 4H, 6), 4.25–4.37 (t, 4H, 5.5)

The figures in parentheses are type of signal, No. of protons, and J values in Hz.

2.4. Suspension polymerization

$MgCO_3$ (0.4 g) and distilled water (100 ml) were taken in a flask fitted with magnetic stirrer, thermometer, dropping funnel and condenser and heated to 80°. Benzoyl peroxide (0.05 wt%) was dissolved in monomer alkyl 2-bromoacrylate (10 g) and added dropwise to the contents of the flask. After complete addition, the reaction mixture was stirred at 80–90° for 1 hr. Conc. H_2SO_4 (0.3 g) was added to neutralize $MgCO_3$. The reaction mixture was cooled and washed with water until neutral. After adding CH_3OH (100 ml), a fine powder of alkyl 2-bromoacrylate polymer was obtained. Suspension stabilizers such as $MgCO_3$ were added to prevent the particles coalescing as the reaction proceeded.

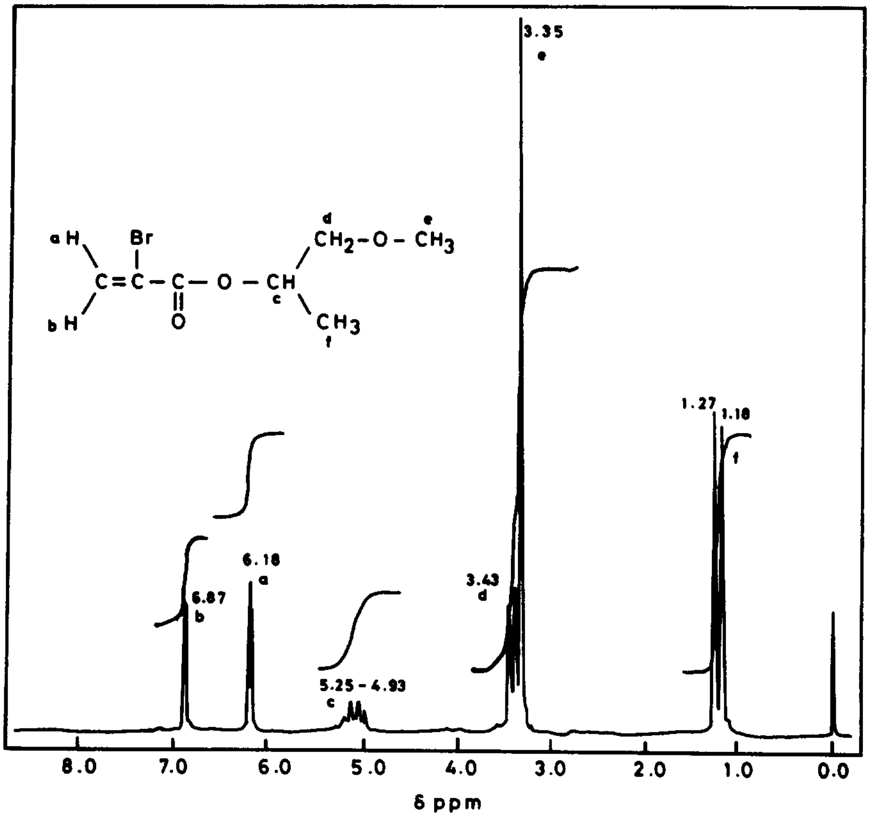


Fig. 1. ^{1}H-NMR spectrum of 2-(1-methoxy propyl) bromoacrylate.

Table 4. ^{13}C-NMR (δ ppm) values of 2-bromoacrylates

Alkyl (R)	δ ppm values of carbons in alkyl chain
Methyl	53.26
Bromethyl	27.95, 65.36
Benzyl	68.14, 128.07, 128.40, 128.51, 134.99
Methoxy 2-propyl	16.20, 59.00, 71.97, 74.56
Cyclopentyl	31.87, 46.19, 66.91
	Bis (2-bromoacrylate)
Diethyleneglycol	68.70, 65.45

Table 5. GPC data for poly (alkyl 2-bromoacrylates)

Poly(alkyl 2-bromoacrylates)	$\bar{M}_w$	$\bar{M}_n$	MWD
Methyl	38,200	5120	7.45
Bromoethyl	10,300	2460	4.18
Cyclopentyl	76,060	52,290	1.45
Methoxy 2-propyl	50,250	50,000	10.04
Benzyl	24,480	1780	13.77
2-Bromoallyl	50,030	3520	14.22

Polymers from the monomeric 2-bromoacrylates were prepared by following the above procedure, and their weight-average molecular weights ($\bar{M}_w$), number-average molecular weights ($\bar{M}_n$), and molecular weight distributions (MWD) were determined by gel permeation chromatography (GPC) (see Table 5). From these data, it is clear that poly(cyclopentyl 2-bromoacrylate); polybromethyl and polymethyl(2-bromoacrylates) have narrow molecular weight distributions.

Alkyl 2-bromoacrylates are not as reactive as alkyl 2-cyanoacrylates. The difference is attributed to the difference between cyano and bromo groups in electron-attracting nature. The carbanion formed in anionic polymerization of 2-cyanoacrylates is stabilized by CN and COOR groups, whereas in 2-bromoacrylates, carbanion is stabilized only by the COOR group, as shown in Scheme 5.

This consideration explains the faster polymerization of 2-cyanoacrylates.

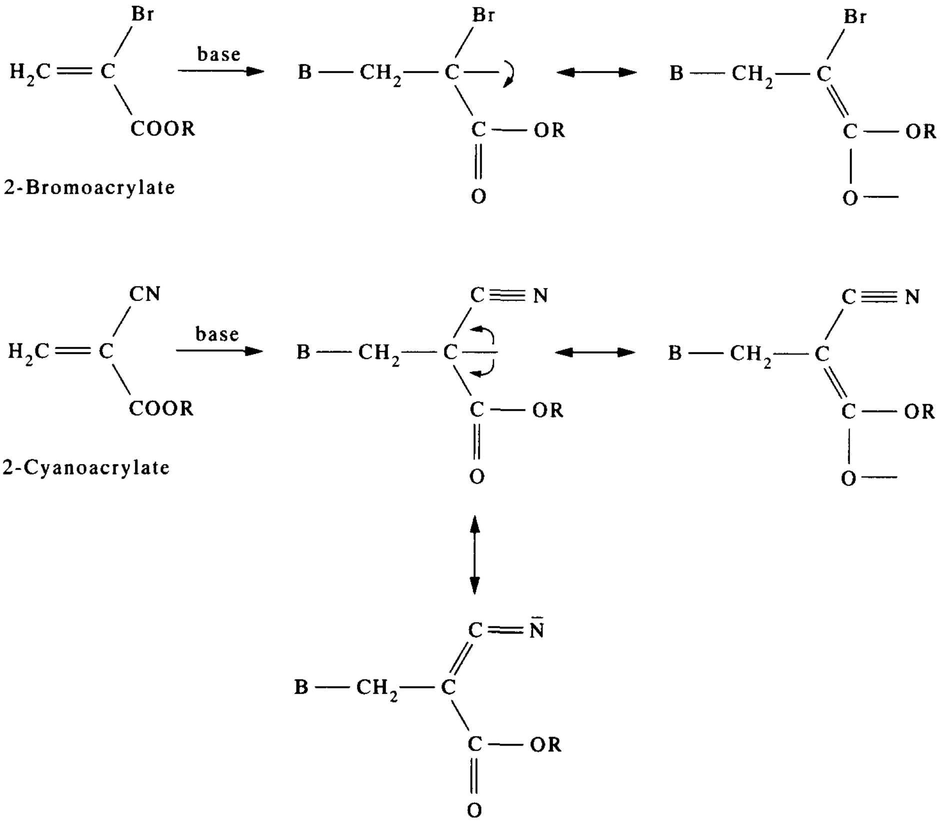
2.5. *Evaluation of 2-bromoacrylates as aerobic adhesives*

Aerobic acrylic adhesives are two-part systems, which offer the advantages of rapid cure and high strength along with good shelf life. The term "aerobic" is used generally to refer to a diminished sensitivity to air inhibition of thick layer curing properties and the ability to cure between two surfaces regardless of the presence or absence of air at room temperature, resulting in tough, elastomeric bonds. These adhesives are generally premix and require the use of pre-applied activators to initiate the cure mechanism. This property is distinct from anaerobic adhesives, which are intrinsically single component products and will polymerize in the absence of air.

Various aerobic adhesive compositions were made from alkyl 2-bromoacrylates and diethyleneglycol bis(2-bromoacrylate). Their tensile bond strengths were determined using the Hounsfield tensiometer between metal surfaces according to ASTM D-897-78 specifications.

A two-part adhesive composition consists of a solution of acrylic monomer, polymerization catalyst and inhibitor in the first part, and an activator in the second part. A typical composition is given below:

	Ingredients	Parts by weight
Part one	Monomer (2-bromoacrylate)	5.000
	Saccharin	0.200
	Cumene hydroperoxide	0.050
	Hydroquinone	0.025
Part two	Activator (*N*,*N*-dimethyl *p*-toluidine)	0.025



Scheme 5

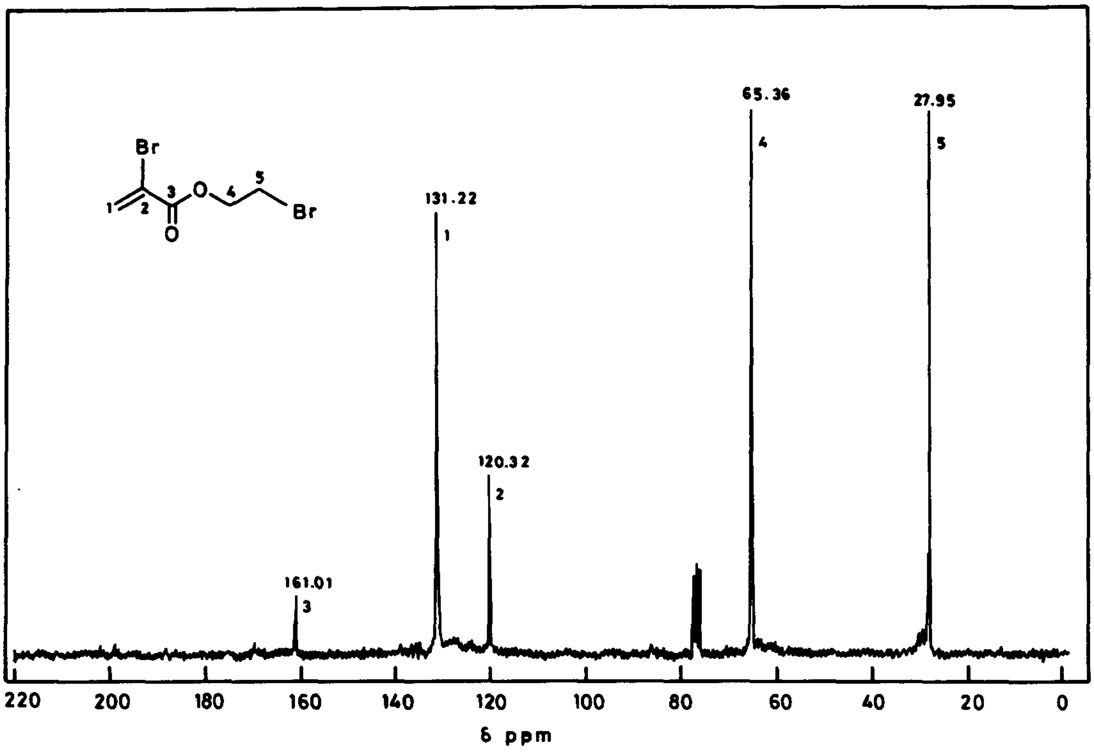


Fig. 2. ^{13}C-NMR spectrum of bromoethyl 2-bromoacrylate.

Using the quoted quantities, aerobic adhesives were prepared using methyl, bromethyl, 2-bromoallyl, cyclopentyl, methoxy-2-propyl, acetoxyethyl and benzyl 2-bromoacrylates and ethyleneglycol bis(2-bromoacrylate).

First, the activator was applied as a thin film to one of the surfaces to be joined and the adhesive was applied to the other mating surface. The two surfaces were brought together and bonded. The glued specimens were left for 24 hr at room temperature (25°), and tested for resistance to a uniform direct pull. Setting time and tensile shear strength of aerobic adhesives are given in Table 6.

It has been found that, with increase in the amounts of saccharin and dimethyl *p*-toluidine (DMPT), the set-time decreased. Too much activator lowered the bond strength. The quantity of stabilizer could be increased to a certain extent to make the compositions more stable. In all cases,

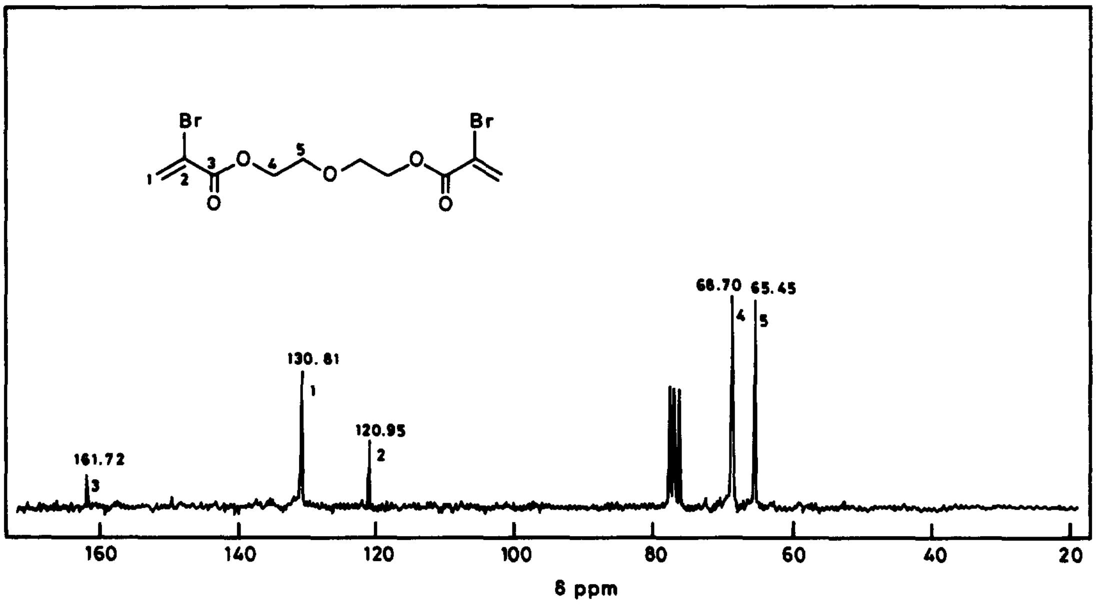


Fig. 3. ^{13}C-NMR spectrum of diethyleneglycol bis(2-bromoacrylate).

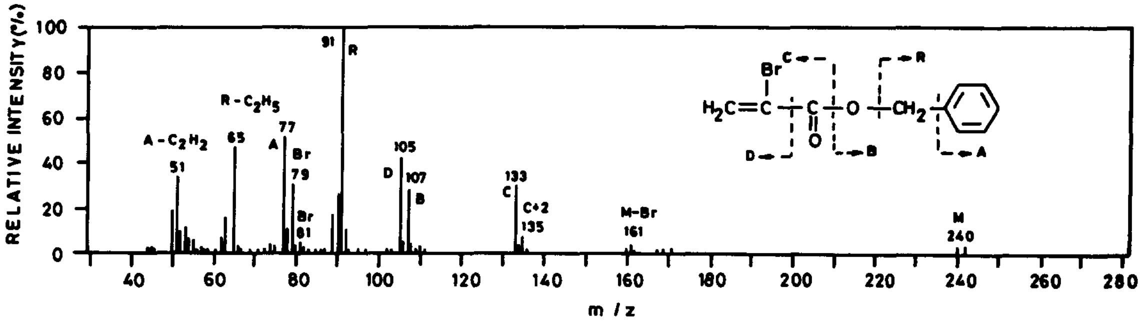


Fig. 4. Mass spectrum of benzyl 2-bromoacrylate.

Table 6. Setting times and tensile strengths of alkyl 2-bromoacrylate bonds between metal surfaces

Alkyl 2-bromoacrylate	Setting time (min)	Tensile strength (MPa)				
		M–M	S–S	A–A	C–C	B–B
Methyl	15	7.03	5.31	2.28	2.20	3.82
Acetoxy ethyl	18	4.92	4.20	2.42	1.84	2.90
Methoxy 2-propyl	20	5.64	4.24	2.64	1.94	3.24
2-Bromoethyl	12	4.42	3.78	2.08	1.98	3.18
Cyclopentyl	20	3.79	3.74	1.82	1.80	2.28
Benzyl	15	2.28	1.52	1.04	1.02	1.50
2-Bromo allyl	10	9.31	6.41	4.24	3.22	4.28
	Bis (2-bromoacrylate)					
Diethyleneglycol	10	8.08	6.04	3.04	2.52	3.79

M, Mild steel; S, stainless steel; A, aluminium; C, copper; B, brass.

the adhesive bond strength was highest between mild steel surfaces followed by stainless steel, brass, aluminium and copper. The aerobic adhesive composition based on 2-bromoallyl 2-bromoacrylate and diethyleneglycol bis(2-bromoacrylate) gave highest adhesive bond strength between the metal surfaces, because of the crosslinking between the unsaturated groups.

3. CONCLUSIONS

Alkyl 2-bromoacrylates were found to be useful in aerobic adhesive formulations, giving good adhesive bond strengths between various metal surfaces. Of these alkyl 2-bromoacrylates, 2-bromoallyl 2-bromoacrylate and diethyleneglycol bis(2-bromoacrylate) gave stronger adhesive bonds because of the crosslinking taking place in the polymers.

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