SYNTHESIS AND CHARACTERIZATION OF SOME POLYFUNCTIONAL THIOALKYLENE ACRYLATE MONOMERS AND THEIR POLYMERS—I

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Abstract—New polyfunctional thioalkylene acrylate monomers have been synthesized by the interaction of β -chloroethylacrylate or methacrylate with sodium mono- or polysulphide. Their physical and chemical properties were determined. It was found that the nucleophilic substitution power of the (S_xNa)⁻ anion increases with increase in the number of sulphur atoms in the anion. It has been established that peroxides cannot initiate polymerization of the monomers. Oxidation-reduction initiators such as (Na₂S₂O₈ + NaHSO₃) lead to crosslinked polymers which possess relatively low glass temperatures, high degree of elasticity and stability towards solvents and heat.

INTRODUCTION

THE PRESENCE of sulphur atoms in a polymer chain leads to increased flexibility of the molecule, so affecting elastic properties.

The activation energies for rotation around C—S, C—O and C—C bonds are 2.0, 3.7 and 3–4 kcal/mole, respectively.⁽¹⁾ Consequently, rotation around the C—S bond occurs more readily than rotation around C—O and C—C bonds.

Sulphur-containing polymers possess elastic properties superior to those of the corresponding carbon and oxygen-containing polymers. There is also a decrease in the glass temperature.

Acrylic polymers with sulphur in the side chain have been synthesized,^(2,3) they are elastomers with low glass temperature, high stability towards solvents and low degree of swelling.

The increase in hardness due to the presence of polar sulphide bonds is compensated by the decrease in the energy barrier for rotation around these bonds.

In addition, the thioether group (C--S--C) possesses an inhibition effect on the peroxide radical formed by the action of heat and light during fabrication and use of the polymer. Accordingly, the sulphur-containing polymers must be thermally stable than their corresponding carbon and oxygen analogues. This inhibition effect can be explained by the high electron density on the sulphur atom.

Sulphur-containing polymers possess relatively high stability towards water and humidity. This was proved experimentally in the case of thiomethylene polymer $-(-CH_2-S-)_n$, which is stable towards water, while its oxygen-containing analogue polyoxymethylene $-(CH_2-O_{n-})_n$ when *n* is small is soluble in water. This behaviour can be explained by the ease of hydrogen bond⁽⁴⁾ formation between water molecules and polyoxymethylene. For polythiomethylene, such hydrogen bonding does not occur.

Marvel,^(5,6) Reppe,^(7,8) Koton and Kiseliva⁽⁹⁾ have synthesized a number of sulphurcontaining polymers by different methods. The latter authors studied the influence of the replacement of oxygen in methacrylic acid esters by sulphur on their ability to polymerize.

The aim of the present investigation is to synthesize some thermally stable crosslinked polymers having elastomer properties.

It is proposed that a sulphur atom in the acrylate ester chain will affect the physical, chemical and mechanical properties of the resulting crosslinked polymers.

EXPERIMENTAL

Infra-red spectra were measured on Carl Zeiss V.R-10 using KBr for the region 400-700 cm⁻¹, NaCl for the region 800-1800 cm⁻¹ and LiF for the region 2880-3400 cm⁻¹.

Synthesis of diacrylate or dimethacrylate diethylene sulphide

The diacrylate diethylene sulphide (AES) and dimethacrylate diethylene sulphide (MES) were prepared by the interaction of β -chloroethylacrylate or methacrylate with Na₂S in dimethyl formamide or a mixture of alcohol and water.

In a 3-necked flask with stirrer and thermometer was placed 0.5 mole of 50% solution Na₂S in water at 50°. Then dimethylformamide or water was added with β -chloroethylacrylate or methacrylate (1.1 mole) in equal amounts. Hydroquinone (1% by weight of β -chloroethylacrylate) was added to inhibit polymerization during synthesis. The reaction mixture was heated for 2 hours at 70°, cooled to room temperature, and toluene was added as a solvent. The reaction mixture then washed with saturated aqueous NaCl solution, followed by 5% Na₂CO₃ solution, and finally with water. The toluene layer was separated, dried (Na₂SO₄) and toluene was then distilled *in vacuo*, first at 11-15 mm/Hg and then at 1-2 mm/Hg for complete removal of the unreacted ester. The monomers were purified by running their toluene solutions through Al₂O₃ (activated at 450° for 1 hr). The disadvantage of this process of purification is the loss of much monomer by absorption on Al₂O₃. Yields of the pure monomers were 32-45 per cent.

Synthesis of diacrylate or dimethacrylate diethylene polysulphides

Diacrylate- or dimethacrylate diethylene di- and tetrasulphides AEDS, MEDS, AETS and METS were similarly synthesized by the method used for the preparation of AES and MES, using Na_2S_2 and Na_2S_4 instead of Na_2S .

Sodium di- or tetrasulphides⁽¹⁰⁾ were prepared as in the literature. The diacrylate- or dimethacrylate diethylene di- and tetra-sulphides were separated and purified as in the case of AES and MES monomers.

These acrylic monomers cannot be distilled because of decomposition during distillation.

Synthesis of β -chloroethylacrylate or methacrylate

In a 3-necked flask fitted with a stirrer, thermometer and reflux condenser and a trap for removal of separated water, a mixture of $1 \cdot 1$ mole of acrylic or methacrylic acid and 1 mole of ethylene chlorohydrin dissolved in (100% solution) toluene was placed. *p*-Toluene sulphonic acid was added as catalyst (4 per cent of the weight of the reacting components) and 1% hydroquinone (based on the weight of acrylic acid) was added as inhibitor of polymerization. The reaction mixture was heated at the b.p. of the solvent; the esterification was followed by the amount of water separated. When the reaction was complete (3-4 hr), the reaction mixture was cooled to room temperature, treated with aqueous 5% Na₂CO₃ solution and washed with water. The toluene layer was dried and distilled under vacuum; the yield was 70-75 per cent. Table 1 shows the physical properties and analyses of β -chloroethyl methacrylate and dimethacrylate ethylene glycol.

The fundamental physical and chemical properties of the synthesized monomers are shown in Table 2. Their i.r. spectra show bands in the regions 1680 cm⁻¹, 1730–1717 cm⁻¹, 3120 cm⁻¹, 2890 cm⁻¹, 700–600 cm⁻¹, and 500–400 cm⁻¹, characteristic for C=C, C=0, =CH₂, C-H, C-S, S-S groups, respectively.

Polymerization

(a) *Emulsion polymerization*. The monomers were polymerized by heating in a sealed tube for 4 hr at 50° in the presence of oxidation-reduction initiator $(Na_2S_2O_8 + NaHSO_3)$ using the following system: 100 g monomer, 18 g H₂O, 5 g emulsifier, 1 g. $Na_2S_2O_8$, 1 g NaHSO₃.

TAB	le 1. Physic	CAL AND CH	EMICAL PR	OPERTIES O	F β-CHLOROE	тнуг метна(RYLATE AN	ND DIMETHA	CRYLATE ETHYLI	ENE GLYC	J	
		2	þ. þ.	W*	Ro	Four	% pr			రో	ilculated	~
Ester	4	DD DD	<u>(</u>)	Found	Calc.	U	Н	σ	r Utiliuia	U	Н	α
3-Chloroethyl methacrylate	1 · 105	1-4515	60 (7·5)	35-43	34-23	48•2	5.89	23 • 1	C ₆ H ₉ O ₂ Cl	48.6	6.08	23.9
Dimethacrylate ethylene glycol	1.035	1 • 4553	mm/Hg 85 (2) mm/Hg	50 -66	50-75	60.1	6.18	1	C ₁₀ H ₁₄ O ₄	60.6	7.07	1

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efraction)
molecular r
* <i>MR</i> ¹¹ (1

where M = molecular weight, d_4^{20} = density and n_D^{20} = refractive index.

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QX	Monomer	ء ج	d ²⁰	A20	Este (mg ×	r no. KOH/1g)	ĨŴ	¢_p	Mole wei	cular ght	Ŭ	~	H	%	S.	~
		(°C)	4	<i>a</i> ,	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
-	AES	150–156 (2 mm/Hz)	1.113	1.4880	565	520	58-44	59-2	230	258	52-2	52-0	6.09	6.11	13-91	13-54
7	MES	170–178 2 mm/Hr)	, 1 · 101	1-4865	435	478	67-21	67 • 71	258	268	55.8	55-4	6.98	7.10	11.78	11・46
، س	AEDS		1.285	1.5719	1	!	66·13	67-84	262	286	45.8	45.6	5.34	5.60	24-42	24·21
4 40	MEDS [*]		1·22 1·34	1 • 5597 1 • 5981			75·37 81·51	75.6 81-09	326 326	280 345	49.65 36.8	49-42	6·21 4·20	6.47 4.51	22-10 39-55	21-85
91	METS*		1.308	1.5943		1	90.81	9.06	354	375	40-65	40.42	2.09	5.34	36.15	35.88
-	MEG (3	135 mm/Hg)	690-1	1964-1	463	404	61-63	19.09	242	251	59-5	59-2	7.4	7.3	1	I
+ YE	$S = CH_{2^{-1}}$	=C-C00(CH2CH2	S CH ₂ CH	-00C-	C=CH ₂ ;	MES	CH ₁ =C	000	H ₂ CH ₂ S	CH ₂ CH	000	-CH2			
		-н						-0	I.			-0	H3			
ΑI	iDS ≡ CH		OCH ₂ CH	I ₂ S ₂ CH ₂ C	3H200C		2; MED	S ≡ CH ₂		00CH3C	H ₂ S ₂ CH	CH2000	J-	CH,		
		H				H			CH3				CH3			
AI	STS ≡ CH	2=CCOC) CH₂CH	l ₂ S4CH2C	H200C	HO-CH	2; MED	$S = CH_2$	О 	00CH2CI	H ₂ S4CH3	CH ₁ 00C		.Н		
		H				-H			ĊH₃				ĊH3			
† M	onomers 3,	4, 5 and 6 u	indergo d	lecomposi	tion witl	h eliminati	on of sul	phur whe	n heated	to 170-18	0° at 1-3	mm/Hg v	acuum.			

TABLE 2. PHYSICAL AND CHEMICAL PROPERTIES OF THIOALKYLENE ACRYLATE MONOMERS

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			TABLE 3			
Polymer	AES	MES	AEDS	MEDS	AETS	METS
Yield	33.4	31.8	25.3	22 · 1	19.5	17.7

The polymers were precipitated and washed several times with methanol, then dried under vacuum to constant weight. Polymers of AEDS, MEDS and METS are odourless, yellowish paste-like materials; those obtained from AES and MES are odourless, yellowish fine powders, insoluble in acetone, chloroform, toluene, carbon tetrachloride but swelling in acetone. This indicates that these fine-grain polymers are crosslinked.

(b) Polymerization in bulk. Trials for polymerization of these monomers in bulk using vacuum sealed tubes at 60° for 12 hr in the presence of 1.5% azobisisobutyronitrile were successful only for monomers AES and MES, with yields 27 and 25 per cent, respectively. The other monomers did not polymerize under these conditions. The analytical data (cf. Table 4) confirm their structure.

NT-	Delamas	Polymeriz-	С	%	H	[%	S	%
NO.	of	process	Calc.	Found	Calc.	Found	Calc.	Found
1	AES	Bulk	52.2	52.60	6.09	6.03	13-91	13.50
2	MES	Bulk	55.8	55.90	6.58	6.87	11.78	11.32
3	AEDS	Emulsion	45.8	46.10	5.34	5.12	24.42	24.35
4	MEDS	Emulsion	49.65	50 · 10	6.21	6·08	22.1	22·07
5	AETS	Emulsion	36.8	36.85	4.29	4.14	39.55	39.00
6	METS	Emulsion	40.65	40.90	5.09	4.98	36.15	35.90

TABLE 4. ANALYSES OF THE POLYMERS

DISCUSSION

The interaction of sodium sulphides with β -chloroethyl acrylate or methacrylate can be considered as a nucleophilic substitution reaction:

where x = -H, $-CH_3$ and y = 1, 2, 4.

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Data in Table 5 indicate that the yields of the monomers increase with increase of the number of sulphur atoms in the anion $(S_yNa)^-$, i.e. increase in the number of sulphur atoms favours the nucleophilic substitution reaction due to the high electron density on the $(S_yNa)^-$ anion.

			TABLE 5			
Monomers	AES	MES	AEDS	MEDS	AETS	METS
Yield	34.8	32.3	39.5	37.3	45.9	45.1

The relatively poor yield of the monomers (30-45%) (cf. Table 5) may be due to either the absorption on Al₂O₃ as previously mentioned (p. 688) or to the low equilibrium constant for the reaction under consideration. If the reaction takes place in aqueous solution, hydrolysis leads to degradation for both the starting and the produced esters as follows:

(a)
$$CH_2 = C - COO - CH_2CH_2S_yCH_2CH_2OOC - C = CH_2 + 2 OH^-$$

 \downarrow
 x
 $2 CH_2 = C - COO^- + 2 HOCH_2CH_2S_yCH_2CH_2OH$
 \downarrow
 x
(b) $CH_2 = C - COOCH_2CH_2CI + OH^- - CH_2 = C - COO^- + HOCH_2CH_2CI$
 \downarrow
 x
where $x = -H$, $-CH_3$
 $y = 1, 2, 4$.

The i.r. spectra of AES (I), MES (II) and dimethacrylate ethylene glycol (III) show that the absorption bands due to the double bond are weaker than those for the corresponding oxygen-containing monomers (see curves, I, II and III in Fig. 1). This effect may be due to the formation of intermolecular donor-acceptor associations between the sulphur atom of one molecule with the double bond of another molecule thus:



It was found that peroxides do not initiate polymerization of these monomers; this

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FIG. 1. Infra-red spectra (I) diacrylate of diethylene sulphide; (II) dimethacrylate of diethylene sulphide; (III) dimethacrylate of ethylene glycol.

failure can be explained by the interaction of the sulphur atom in the monomer with peroxidic compounds:

$$ROOH + R' - S - R' \longrightarrow \begin{bmatrix} ROOH \\ \uparrow \\ R' - S - R' \end{bmatrix} \longrightarrow ROH + R' - S - R'$$

The resulting complex has no tendency to break down with the formation of radicals and, therefore, cannot initiate polymerization.

In the case of oxidation-reduction initiators $(Na_2S_2O_8 + NaHSO_3)$, the resulting ion-radicals cannot approach close to the sulphur atoms because of the negative charge.

This suggestion was partially indicated by the i.r. spectra of the resulting polymers. In these spectra, the absorption band characteristic for the S=O group (1050 cm⁻¹) is absent (see Fig. 2).



FIG. 2. Infra-red spectrum of polymer.



Fig. 3. Studies on thermal stabilities of polymer. (1) and (2) sulphur-containing polymers; (3) polydimethacrylate diethylene glycol.



FIG. 4. Glass-transition temperatures for polymers of AES (1) and MES (2).

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The i.r. spectrum of polydimethacrylate diethylene sulphide confirms the suggested structure. The absorption bands for the various groups are less sharp than those for the corresponding monomers.

Thermal stability of polymers derived from AES and MES was examined using an automatic thermal balance at 200° in oxygen. For comparison, polydimethacrylate diethylene glycolwas also examined as an oxygen-containing analogue under the same conditions (see Fig. 3). From these curves, it is obvious that the oxygen-containing substance (curve 3) undergoes destruction more vigorously (50 per cent loss in weight) than the corresponding sulphur-containing polymers (25 and 30 per cent losses respectively) (curves 1, 2). The glass temperature of polymers derived from AES and MES were $+40^{\circ}$ and $+3^{\circ}$, respectively (see curves 1 and 2 in Fig. 4).

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Résumé—On a effectué la synthèse de nouveaux monomères polyfonctionnels acrylate de thioalkylène, par l'interaction des β chloroéthylacrylate ou méthacrylate avec le mono- ou le polysulfure de sodium. On a déterminé leur propriétés physiques et chimiques. On a trouvé que le pouvoir de substitution nucléophile de l'anion (S_xNa)⁻ augmente avec le nombre d'atomes de soufre dans l'anion. On a établi que des peroxides ne pouvaient pas amorcer la polymérisation de ces monomères. Des amorceurs d'oxido-réduction tel que (Na₂S₂O₈ + NaHSO₃) conduisent à des polymères réticulés qui ont des températures de transition vitreuse relativement basses, un degré élevé d'élasticité et une bonne stabilité vis à vis des solvants et de la chaleur.

Sommario—Mediante interazione di β -cloroetilacrilato oppure matacrilato con mono- o polisolfuro di sodio, si sono sintetizzati dei nuovi tioalchilene acrilati monomeri polifunzionali. Si sono determinate le loro caratteristiche fisiche e chimiche. Si è trovato che la forza di sostituzione nucleofilica dell'anione (S_xNa)⁻ aumenta con l'aumentare del numero di atomi di zolfo nell'anione Si è potuto stabilire che i perossidi non possono iniziare la polimerizzazione dei monomeri. Iniziatori ossidanti-riducenti come (Na₂S₂O₈ + NaHSO₃) portano alla formazione di polimeri a legami incrociati i quali posseggono temperatura di passaggio vetroso relativamente basse, un alto grado di elasticità e stabilità nei confronti di solventi e calore.

Zusammenfassung—Durch Reaktion von β -Chloräthyl-acrylat oder -methacrylat mit Natriummonooder polysulfid wirden neue Thioalkylenacrylat Monomere synthetisiert. Ihre physikalischen und chemischen Eigenschaften wurden bestimmt. Es wurde festgestellt, da β die Stärke der nucleophilen Substitution des (S_xNa)⁻ Anions mit steigender Zahl der Schwefelatome im Anion zunimmt. Es stellte sich heraus, da β die Polymerisation der Monomeren nicht durch Peroxide initiiert werden kann. Oxidations-Reduktions Initiatoren wie (Na₂S₂O₈ + NaHSO₃) führen zu vernetzten Polymeren mit relativ niedrigen Glastemperaturen einem hohen Grad der Elastizität und der Stabilität gegen Lösungsmittel und Wärme.