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THE SYNTHESIS AND CHARACTERISATION OF 2–MERCAPTOETHYL METHACRYLATE

The synthesis of 2–mercaptoethyl methacrylate from methacrylic acid and 2–mercaptoethanol by esterification using acetyl chloride as catalyst was optimised. The purity of the obtained product was controlled by gas chromatography and its identity confirmed by ^{1}H–NMR and FTIR spectroscopy. 2–Mercaptoethyl methacrylate could find application as a chain transfer agent in radical polymerisations.

Thiols, halogenated hydrocarbons and phenols are well known transfer agents utilised in radical polymerisation to adjust the molar mass of the resulting polymer [1]. The mechanism of chain transfer to thio–compounds may be presented in the following fashion [2]:

$$RM_n\cdot + HS–F \rightarrow RM_n–H + F–S\cdot \quad (1)$$

$$F–S\cdot + M \rightarrow F–S–M\cdot \quad (2)$$

where $RM_n\cdot$ is a macroradical and HS–F a thiol.

Chain transfer to a thiol occurs when a monomer molecule is not added to a propagating macroradical but a chain transfer agent releases its hydrogen and terminates the growth of the macroradical. The formed thio–radical can start the propagation of a new polymer chain. Such a transfer reaction causes a decrease in the degree of polymerisation. In most cases the chain transfer rate constant increases with temperature. The chain transfer constants to some thio–compounds during the radical polymerisation of methyl methacrylate (MMA) are presented in Table 1 [3].

More recently, thiols have been applied to prepare and/or stabilise colloidal semiconductors and nanoclusters [4,5]. The goal of this study was to synthesise a dual–purpose monomeric chain transfer agent. The compound could be applied as a chain transfer agent and incorporated into a polymer providing it with predominantly chain–end unsaturation. It could also be used as a thio–stabiliser for colloidal nanoparticles which would subsequently be polymerised with the addition of an initiator and a selected monomer.

Table 1. Chain transfer constants of thio–compounds, in the temperature interval 40°C–100°C, during the polymerisation of MMA [3]

Thio–compound	Chain transfer constant, C_T
2–mercaptoethyl acetate	0.62
2–mercaptoethanol	0.62
2–propane thiol	0.38
1–butane thiol	0.67
1–pentane thiol	0.80
benzene thiol	2.7
2–naphthene thiol	3.0

EXPERIMENTAL

2–Mercaptoethyl methacrylate was synthesised by esterifying methacrylic acid with 2–mercaptoethanol, using freshly distilled acetyl chloride (Ac–Cl) as a catalyst. Due to the possibility of simultaneous ester and thio–ester formation, as well as other side reactions, the synthesis had to be strictly controlled in terms of reaction temperature and time. The synthesis conditions were varied in order to optimise the yield of 2–mercaptoethyl methacrylate, Table 2.

The molar ratio of the reactants methacrylic acid and 2–mercaptoethanol was 1:3. Methacrylic acid, 2–mercaptoethanol and a pinch of hydroquinone were added to a 250 ml three–necked flask equipped with a combined Vigreux column and Liebig condenser, thermometer and septum and heated under constant stirring. Acetyl chloride was injected when the temperature in the flask reached 50°C, after which an immediate temperature increase was registered. The temperature in the flask was further increased to the selected reaction temperature and maintained for the predetermined time, upon which Ac–Cl was removed from the system by water vacuum distillation together with a part of the unreacted alcohol. The contents of the flask were cooled to room temperature and diluted with solvent. The obtained mixture was washed several times with a 10 mass.% aqueous solution of NaOH in a separating funnel and subsequently rinsed with distilled water. The organic phase was dried overnight over anhydrous $CaCl_2$. The solvent was removed by distillation. The crude pro-

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Table 2. Conditions for the synthesis of 2–mercaptoethyl methacrylate

Component	No. 1	No. 2	No. 3	No. 4	No. 5
Methacrylic acid (mol)	0.5	0.25	0.25	0.25	0.25
2–Mercaptoethanol (mol)	1.5	0.75	0.75	0.75	0.75
Acetyl chloride (ml)	2	1	2	9 (0.125 mol)*	9 (0.125 mol)*
Reaction temperature (°C)	125	100	100	100	100
Reaction time (min)	10, 30	60	85	70	
Dilution with solvent	–	benzene	benzene	benzene	chloroform
Washing out with aq. NaOH	no	yes	yes	yes	yes

*Added in 1 ml portions, temperature in the flask maintained at 50–60°C

duct was fractionated by vacuum distillation. A clear, viscous yellow liquid was obtained as the final product. The fractions were characterised by gas chromatography, IR and ^{1}H NMR spectroscopy.

Gas chromatography was performed on a Varian 3400 instrument with a FID detector. A capillary DB–5 column of 30 m length and 0.25 i.d. was used. The injector and detector temperatures were 250° and 300°C, respectively, while the following column heating program was applied: 60°C for 5 min, 60–250°C at 5°/min, 250°C for 30 min. IR spectra of samples in KBr pellet form were recorded on a BOMEM MB series instrument. A Varian Gemini 200 instrument was used to record the ^{1}H NMR spectra. Deuterated chloroform was used as the solvent and tetramethylsilane as the internal standard.

The monomer was polymerised in bulk in a degassed sealed ampoule at 40°C with 0.7 mol.% of α,α'–azobisisobutyronitrile as initiator for 8 days. The polymer, obtained in low yield, was precipitated in methanol containing 10 vol.% of distilled water and dried to constant mass. The polymer was characterised by gel permeation chromatography (GPC) on a Waters instrument with a RI detector. THF was used as the solvent and a calibration based on polystyrene standards (Polymer Laboratories) was applied.

RESULTS AND DISCUSSION

2–Mercaptoethyl methacrylate was synthesised by esterifying methacrylic acid with 2–mercaptoethanol. Reactions yielding thio–ester and mixed esters may also be expected, Figure 1.

The presence of highly reactive groups enables the occurrence of other undesired reactions. Consequently, the monomer was not synthesised in high yield and with satisfactory purity. The first fraction of the product of synthesis No. 5 was obtained in the highest yield and further characterised. The critical temperatures and normal boiling points of the major expected products were calculated according to the Fedors and Joback methods, respectively, Table 3 [6]. The compounds were identified by GC, based on their retention times and normal boiling points. The composition of the product is presented in Table 4.

Analysis of the IR spectrum of fraction 1 of synthesis No. 5 revealed the presence of characteristic peaks for the structure of 2–mercaptoethyl methacrylate, specifically the S–H stretching vibration at 2560 cm^{-1}, the carbonyl stretching frequency at 1738 cm^{-1}, the C–O stretching vibration in esters at 1233 cm^{-1}, as well as the carbon–carbon double bond at 1653 cm^{-1}. Analysis of the ^{1}H NMR spectrum of fraction 1 of synthesis No. 5 is presented in Table 5.

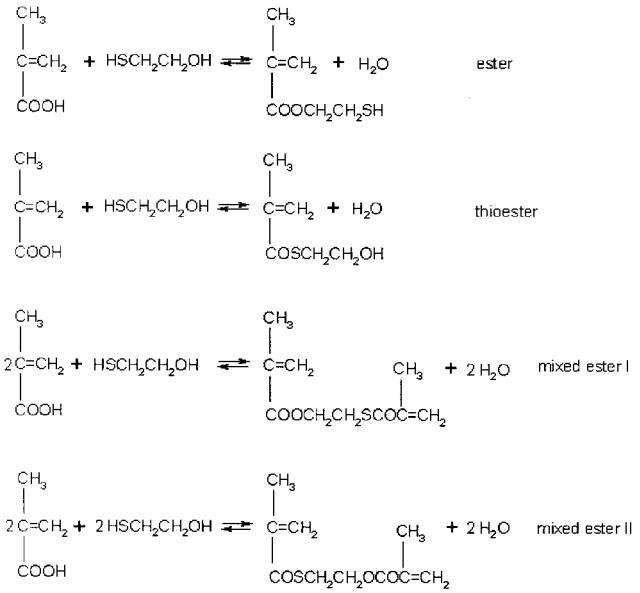

Figure 1. Products of the esterification of methacrylic acid with 2–mercaptoethanol

Table 3. Calculated critical temperatures, T_c, and normal boiling points, T_b, of the expected synthesis products

Compound	T_c (K)	T_b (K)	T_b (°C)
2–Mercaptoethyl methacrylate	666.7	459.8	186.7
2–Hydroxyethyl thiomethacrylate	727.1	535.3	262.2
Mixed ester I	764.1	567.3	294.2

On the basis of the GC, IR and ^{1}H NMR results, it may be concluded that the major product of the esterification of methacrylic acid with 2–mercaptoethanol is 2–mercaptoethyl methacrylate. In a preliminary investigation of this monomer as a transfer agent, the crude monomer was polymerised in bulk and the obtained product characterised by GPC. The molar mass of the product was low, $\overline{M}_n$ = 1250 g/mol with a polydispersity of approxi-

Table 4. Composition of fraction 1 of synthesis No. 5 based on GC

Peak no.	Compound	Retention time (min)	Amount (wt.%)
1	2–mercaptoethyl methacrylate	8.6	78.9
2	2–hydroxyethyl thiomethacrylate	13.4	6.7
3	mixed esters	14.2	14.4

mately 1, implying that an oligomer was formed due to extensive transfer reactions.

The chain transfer constant to monomer, CM, was approximated by the Mayo equation [7]

$$\frac{1}{\overline{X}_n} = \frac{1}{\overline{X}_{n,0}} + \frac{k_{tr,X}}{k_p} \cdot \frac{[X]}{[M]} \qquad (3)$$

where: $X_{n,0}$ – is the number–average degree of polymerisation assuming no transfer reactions took place, [X] – the monomer, initiator, solvent or transfer agent concentration, $k_{tr,M}$ – the rate constant of chain transfer to monomer, and k_p – the rate constant of propagation.

It was assumed that chain transfer to monomer occurred, while chain transfer to initiator was considered to be negligible. It was also postulated, for the purposes of a rough approximation, that no transfer to polymer took place. Thus, equation (3) simplified to the form

$$C_M = \frac{k_{tr,M}}{k_p} \approx \frac{1}{\overline{X}_n} \qquad (4)$$

The approximation yielded a value of $C_M = 0.12$. Considering: a) the purity of the compound that was polymerised, b) the possibility of other compounds present in the crude product to initiate transfer reactions and c) that the formed oligomer itself can initiate transfer reactions due to the presence of mercapto–groups in the ester substitients, the obtained value of C_M can only indicate that the order of magnitude of the constant is the same order as those of the thio–compounds presented in Table 1. The chain transfer constant to monomer for most standard methacrylate monomers at 60°C is about $C_M \approx 10^{-5}$ [3].

Table 5. Analysis of the ^1H NMR spectrum fraction 1 of synthesis No. 5

Chemical shift δ, ppm	Signal shape (multiplicity)	Group of atoms assigned to the shift
1.50	triplet	H atom from the –SH group in an alcohol or ester
2.10	singlet	H atoms from the $–CH_3$ group in an ester or thioester
2.75	quartet	H atoms from the $–CH_2–$ group bound to –SH in an ester
4.20	triplet	H atom from a $–CH_2–$ group bound to –O– in an ester
5.60	singlet	H bound to a C atom with a double bond in the trans position to a –COO–group
6.20	singlet	H atom bound to a C atom with a double bond in the cis position to a –COO–group

It may be concluded that 2–mercaptoethyl methacrylate monomer is a promising chain transfer agent that could be applied in the tailoring of polymers or composite materials.

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IZVOD

SINTEZA I KARAKTERIZACIJA 2–MERKAPTOETIL METAKRILATA

(Naučni rad)

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Sinteza 2–merkaptoetil metakrilata esterifikacijom metakrilne kiseline 2–merkaptoetanolom je optimizovana. Čistoća dobijenog proizvoda je kontrolisana gasnom hromatografijom i potvrđena ^1H–NMR i FTIR spektroskopijom. 2–Merkaptoetil metakrilat može da se primeni kao sredstvo za prenošenje aktivnosti lanca u radikalnim polimerizacijama.

Ključne reči: 2–Merkaptoetil metakrilat • Sredstvo za prenošenje aktivnosti lanca • Sinteza • Karakterizacija •

Key words: 2–Mercaptoethyl methacrylate • Chain transfer agent • Synthesis • Characterisation •