

PREPARATION OF INDIVIDUAL BUTYL METHACRYLATE MERS BY ANIONIC OLIGOMERIZATION

J. TREKOVAL

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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The anionic oligomerization of n-butyl methacrylate initiated with sodium n-butoxide in the presence of n-butanol as the polymer chain transfer agent (regeneration of initiator) yielded mono- to tetramers of butyl methacrylate with a high degree of purity.

The possibility of using tert-alkoxides of alkali metals for the initiation of the homogeneous polymerization of methacrylic acid esters has been described in previous papers^{1,2}. The polymerization proceeds in solution and bulk up to a 100% conversion at room temperature. In the presence of tert-alcohol this polymerization leads to chain transfer connected with the regeneration of initiator, and thus also to the regulation of molecular weight. The molecular weight is linearly inversely proportional to the concentration of the tertiary alcohol within the molecular weight range from 120 000 up to oligomers³. This paper reports on the preparation of the individual oligomers (mono- to tetramer) of n-butyl methacrylate by the anionic oligomerization of n-butyl methacrylate with sodium n-butoxide in the presence of a corresponding amount of n-butanol.

EXPERIMENTAL

Chemicals. Butyl methacrylate (a commercial product of Synthesia, Kolín) was freed from inhibitor by shaking with a 2.4% soda solution, washed with water, dried with CaCl_2 and distilled twice on a column with an efficiency of 20 TP under a reduced pressure in argon atmosphere. Butanol was dried over magnesium oxide and distilled.

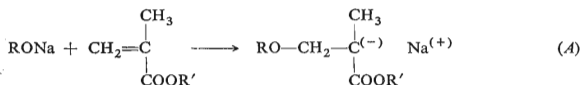
Oligomerization was carried out under argon. Butanol (in an amount calculated according to the chosen oligomer) was dosed into a carefully dried flask, sodium was added (1 to 2% calculated per monomer), and the mixture was heated to boil under a reflux for some two hours. Butyl methacrylate was added on cooling to room temperature, the mixture was thoroughly shaken and then heated to a temperature from 50 to 65°C at which it was maintained for 1–2 h with occasional shaking. On cooling, the reaction mixture was acidified with acetic acid in methanol, washed with water to neutral reaction, dried with CaCl_2 and distilled under a reduced pressure on a column with a 10 TP efficiency. (If the density of the oligomeric mixture used for the preparation of higher mers is higher, it may be diluted *e.g.* by hexane). The yields of oligomers varied around 75% (calculated per monomer and alcohol).

Analytical methods. The molecular weights were determined by the VPO method. The composition of the reaction oligomeric mixture (freed from the alcohol residue and monomer) and the composition of the individual distillation fractions was determined by gas chromatography (a Perkin-Elmer 900 apparatus, column 1.8×2.2 mm packed with Chromosorb W 80-100 mesh with 15% Apiezon L, temperature 220°C ; flow rate of nitrogen 30 ml/min, flame ionization detector) and by gel permeation chromatography (tetrahydrofuran as solvent, flow rate 0.5 ml/min, a system of five columns each 1.2 m long packed with S-gel 232 (prepared in the Institute of Macromolecular Chemistry, Prague), exclusion limit approx. 2.500 mol. weight units, room temperature, detection with a differential refractometer).

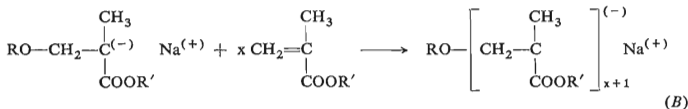
RESULTS AND DISCUSSION

The polymerization of methacrylic acid esters initiated with alkali metals alkoxides in the presence of alcohol proceeds *via* the following partial reactions:

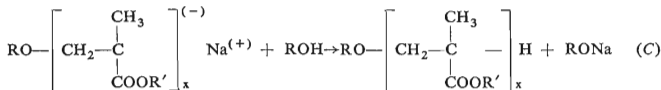
initiation,



growth,



transfer to alcohol (regeneration of initiator)



The growing chain transfer reaction to alcohol with the regeneration of initiator which is capable of initiating further the reaction under given conditions was used for the preparation of *n*-butyl methacrylate oligomers having a high degree of purity (Table I). The use of the same alkyl group in the ester group of the monomer and alkoxide prevented the formation of a complicated product owing to the reesterification reaction between the ester group and alkoxide. Oligomerization under the conditions described above gives a statistic mixture of mers. If the butyl methacrylate : alcohol molar ratio is 3 : 1, which should give rise to a trimer, mono- to hexamer were isolated instead (*cf.* reaction (C), $\text{R}, \text{R}' = \text{C}_4\text{H}_9$, $x = 1-6$); participa-

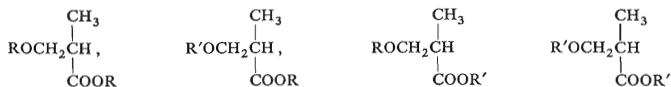
TABLE I
Physical Properties of Mers $C_4H_9O-[CH_2C(CH_3)(COOC_4H_9)]_xH$

x	Boiling point °C/Torr	n_D^{20}	Molecular weight		Purity, %		d_{25}^{25} g.cm ⁻³
			calculated	found ^a	GLC	GPC	
1	59—61/0.1	1.4213	216	218	99.7	99.0	0.89704
2	128—130/0.1	1.4400	358	345	99.0	99.7	0.94360
3	186—190/0.1	1.4508	500	525	—	98.7	0.97355
4	246—250/0.3	1.4574	642	600	—	80.0 ^b	0.99094

^a VPO method. ^b Tetramer contains 0.3% of hexamer, 5.5% of pentamer and 14.2% of trimer; the content of tetramer may be increased considerably by further fractionation.

tion for x 1—4 was 5, 25, 35, and 22 respectively, for $x > 4$ it was 13%. The fact that only oligomer with a normal distribution of the individual mers and no polymer is formed under the given conditions (the mixture of oligomers obtained is not precipitated by precipitating agents for methacrylates) suggests that the tendency of the growing polymer centre to a reaction with the monomer and the hydrogen atom of the alcohol is essentially the same³, and that the composition of the oligomeric mixture thus obtained is given only by the monomer: chain transfer agent (alcohol) ratio. The effect of the amount of the initiator used is negligible.

In principle, two side reactions may take place during the anionic polymerization with alkaline metals alkoxides: 1) Reesterification between the ester group of the monomer or polymer chain on the one hand and alkoxide on the other. If the same alkyl group is used both in the ester group of the monomer and in alkoxide, this reaction does not affect the composition of the product. The alkoxide formed by this reaction is identical with the original one. If the ester and the alkoxide contain different alkyl groups, a mixture is obtained consisting of all products that may be considered in the reaction. Thus, according to gas chromatographic data, the oligomerization of *n*-butyl methacrylate initiated with sodium *tert*-butoxide in the presence of *tert*-butanol gave rise to 3-alkoxy isobutyrate⁴, namely, in the first addition pro-



duct (*cf.* (A)), where R = *n*-butyl and R' = *tert*-butyl. 2) Addition reaction of the growing centre with the ester group of both the polymer and the monomer. The analysis of the products obtained (Table I) shows however that under the given conditions

the reaction of the growing centre with the ester group is in principle negligible. The individual mers may be readily isolated by distillation from the mixture of mers. The boundary between the individual mers observed during the distillation is sharp and without any intermediate fraction, the individual mers exhibit a high degree of purity and contain — as demonstrated by GPC and GLC — only traces of lower or higher mers and no compounds of other type.

The above procedure allows, by using a relatively easy and fast route, the preparation of compounds modelling the first steps of polymerization when the greatest difference between the monomer and the polymer is observed. Oligomers were *e.g.* used for the investigation of the specific polymer–solvent interactions⁵.

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