Polymer Bulletin 27, 511–517 (1992)

Polymer Bulletin

Synthesis and investigation of α,ω-methacryloyl terminated epoxide-amine macromonomers

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SUMMARY

α,ω-methacryloyl-poly(epoxide-amine)-macromonomers were synthesized by reaction of bisphenol-A diglycidylether DGEBA and methacrylic acid followed by addition polymerization of unreacted epoxide groups with primary monoamines or disecondary diamines, respectively. The resultant macromonomers having M_n(vpo)-values between 530 and 2000 g/mol were analysed by IR-, ^{1}H-NMR- and ^{13}C-NMR-spectroscopy. HPLC and GPC analysis were used to determine the distribution of oligomers. The macromonomers are glassy or viscous liquids with T_g between 0 and 50 °C depending on the nature of the amine and polymerization degree.

INTRODUCTION

Macromonomers are linear macromolecules carrying at their chain ends one or two polymerizable groups such as unsaturated units, oxirane rings, oxazole groups and others [1]. Thus, in the last years many papers and review articles [1-3] have been published on the synthesis, properties and oligomer distribution as well as the polymerization of macromonomers to graft copolymers, comblike polymers and networks.
However, methacryloyl-terminated macromonomers are well described from various polymers such as polystyrene [4,5], polyethylene oxide [6,7], polytetrahydrofurane [8] and poly-2(4)-vinylpyridine [9,10].
For some years diacrylates and dimethacrylates of diglycidylethers, especially of DGEBA, applied in electronic and medical technics.
Recently, we reported about the end capping of epoxide-amine prepolymers by reaction with 2,3-(epoxypropoxy)-methacrylate [11].
This paper describes the formation of macromonomers containing epoxide-amine repeating units and methacrylate endgroups. Our purpose was the synthesis of macromonomers with relatively low glass transition temperatures. By combining the mechanical and thermal properties and the good adhesion of epoxide-amine addition polymers with the possibility of the fast radical (photochemical) polymerization of methacrylates and a relatively low shrinking during the polymerization was also aimed at.

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EXPERIMENTAL

Macromonomers **M**:

M-a(n=1, P_n=3): 10,000g (29,38mmol) recrystallized DGEBA, 2,529g (29,38mmol) methacrylic acid, 0,124g tetraethylbenzylammonium chloride and 0,012g hydroquinone were homogeniously mixed under slow heating. The mixture was kept for two hours at 90°C. After this time 1,368g (14,69mmol) aniline was added to the mixture under stirring and kept for additional two hours at 90°C. The obtained macromonomer **M-a** is characterized with: M_n(vpo)=920 g/mol, T_g=27°C.
IR(KBr): 1640, 1730, 3480cm^{-1}
^{1}H-NMR($CDCl_3$, 100MHz): δ=1,50 (6H), 1,83 (6H), 3,58 (4H), 3,92, 4,20, 5,45/6,05 (4H), 6,86 (8H, 8,5Hz)

M-h(n=1, P_n=3): 10,000g (29,38mmol) recrystallized DGEBA, 2,529g (29,38mmol) methacrylic acid, 0,124g tetraethylbenzylammonium chloride and 0,012g hydroquinone were homogeniously mixed under slow heating. The mixture was kept for two hours at 90°C. After this time 5,002g (14,69mmol) N,N'-dibenzyl-5-oxanonanediamine-1,9 was added to the mixture under stirring and kept for additional two hours at 90°C. M_n(vpo)=1200g/mol, T_g=10°C.
Further 6 macromonomers were synthesized in the same manner. Their polymerization degree, M_n(vpo)-, M_n(GPC)- and M_w(GPC)-values and their glass transition temperatures as well are given in tables 1 and 2.

Table 1 Synthesis of α,ω-methacryloyl poly(epoxide-amine) macromonomers **M-a** to **M-h**

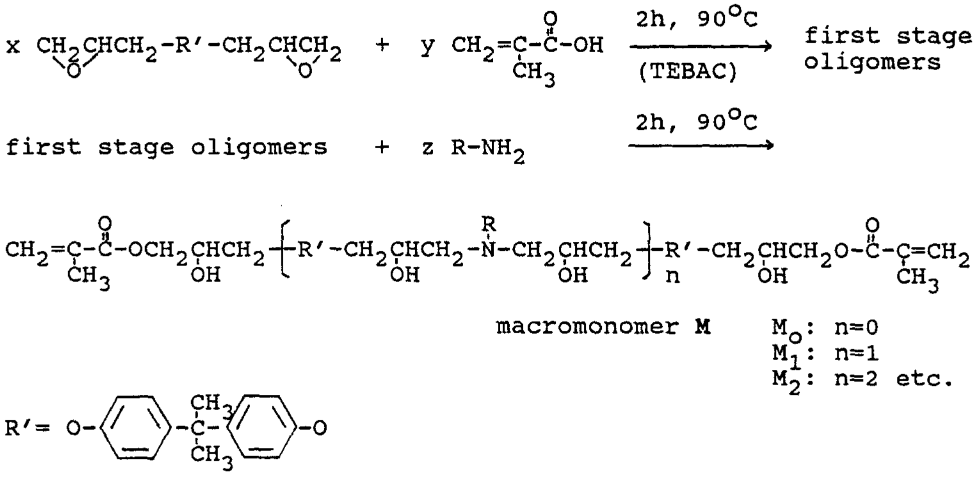
M	R	DGEBA		MAA		Amin		n
		g	mmol	g	mmol	g	mmol	
a	C_6H_5	10,000	(29,38)	4,805	(55,81)	0,137	(1,47)	0,05
b	C_6H_5	10,000	(29,38)	3,793	(44,06)	0,685	(7,35)	0,33
c	C_6H_5	10,000	(29,38)	2,529	(29,38)	1,368	(14,69)	1,0
d	C_6H_5	10,000	(29,38)	1,686	(19,58)	1,824	(19,58)	2,0
e	C_6H_5	10,000	(29,38)	1,264	(14,69)	2,052	(22,03)	3,0
f	$HOCH_2CH_2$	10,000	(29,38)	2,529	(29,38)	0,897	(14,69)	1,0
g	$C_6H_5CH_2$ a)	8,511	(25,00)	2,152	(25,00)	3,004	(12,50)	1,0
h	$C_6H_5CH_2$ b)	17,021	(50,00)	4,304	(50,00)	8,513	(25,00)	1,0

a) N,N'-Dibenzyl-ethylenediamine, b) N,N'-Dibenzyl-5-oxanonanediamine-1,9

The M_n(vpo)-values were determined by vapour pressure osmometry in $CHCl_3$ at 37°C using a Knauer-osmometer. The glass transition temperatures were obtained by DSC 2b (Perkin-Elmer). HPLC and GPC were carried out with Knauer-apparatus, using a RP-18 (5μm) column (250x4mm i.d.), with water/CH_2Cl_2/CH_3OH gradient elution mode and UV detection at 265nm for HPLC.

RESULTS AND DISCUSSION

Macromonomers **M** were synthesized in two steps. At first by reaction of exessive bisphenol-A diglycidylether DGEBA and methacrylic acid MAA (x>2y) an oligomer mixture is obtained. This mixture contains the bismethacrylate of DGEBA (bis-GMA, n=0) along with mono-GMA and unreacted DGEBA as well as governed by the epoxide-amine ratio. The formation of macromonomers **M** follows in a second reaction of primary monoamine with DGEBA and mono-GMA, respectively (eq.1).



The resulting macromonomers are viscous liquids or solids which are soluble in $CHCl_3$, THF, DMF ect. Their glass transition temperatures (tab.2) are relatively low between 0 and 50 °C depending on the nature of the amine and the molecular mass of the macromonomers.

Table 2 Molecular weights and glass transition temperatures of α,ω-methacryloyl poly(epoxide-amine) macromonomers **M-a** to **M-h**

M	n	P_n	M_n(calc.)	M_n(vpo)	M_n(GPC)	M_w(GPC)	M_w/M_n	T_g/°C
a	0,05	1,1	535,6	550	666	818	1,23	-4
b	0,33	1,7	657,1	660	917	1160	1,27	10
c	1,0	3,0	946,2	920	1153	1645	1,43	31
d	2,0	5,0	1379,8	1360	1401	2054	1,47	47,5
e	3,0	7,0	1813,4	1840	1791	2884	1,51	48
f	1,0	3,0	914,1	950	-	-	-	25
g	1,0	3,0	1093,4	1000	-	-	-	22
h	1,0	3,0	1193,6	1200	-	-	-	10

The observed M_n-values of **M-a** to **M-h**, measured by vpo, are in complete accordance with the calculated molecular weights given in table 2. The M_w/M_n-values increases with growing molecular weight of **M** and tend to the value 2 which is expected for high molecular weight addition polymers. Degree of polymerization P_n and macromonomer value n depends on the mol-ratio of the monomers DGEBA and amine and were calulated by $P_n=(1+r)/(1-r)$ and $n=r/(1-r)$, respectively using $r=z/x$.

By means of HPLC analysis (fig.1) these macromonomers **M** were shown to be mixtures of a series of homologous oligomers which components differ by n. The HPLC analysis shows a typical splitting pattern of oligomers with n=1 into two, n=2 into three, n=3 into four signals etc. These splittings are considerable due to the formation of diasteriomeric erythro/threo aminodiol units in course of polyaddition [12].

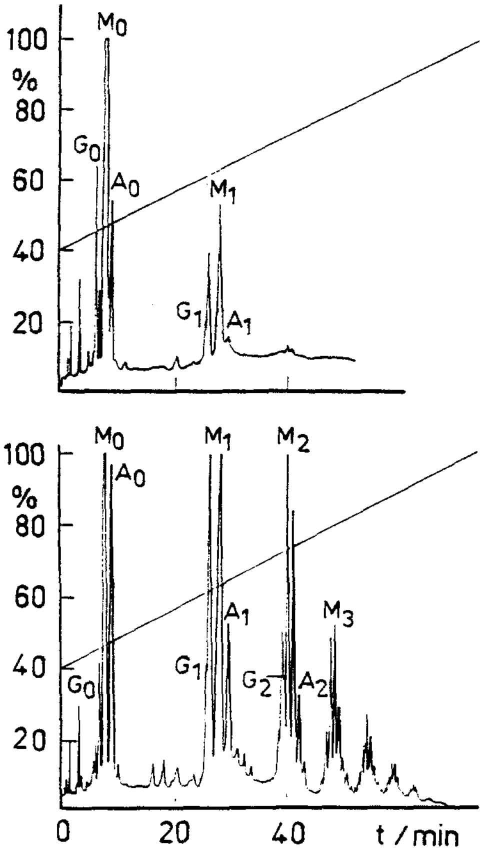
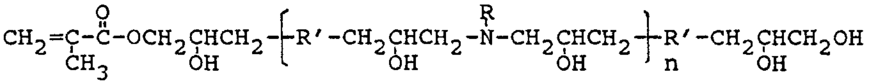


Fig.1 HPLC analysis of macromonomers **M-a** and **M-c**

In HPLC are further two serieses of macromonomers **A** and **G** to be seen.

In presence of quarternary ammonium salts an opening of epoxide rings to glycol units occure in each state of reaction of DGEBA-

MAA and amine. That's why a macromonomer series **G** (fig.1) is formed in less amounts containing glycol units and methacrylate end groups, respectively.

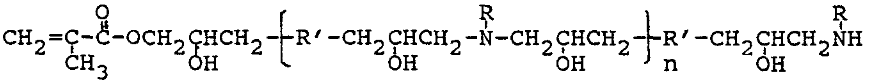


$$CH_2{=}\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-OCH_2\underset{OH}{C}HCH_2-\left[R'-CH_2\underset{OH}{C}HCH_2-\overset{R}{N}-CH_2\underset{OH}{C}HCH_2\right]_n-R'-CH_2\underset{OH}{C}HCH_2OH$$

G

G$_0$: n=0
G$_1$: n=1
G$_2$: n=2 etc.

Consequently, a lesser than the calculated amount of epoxide groups remains to react with amino groups. This gives rise to the formation of further macromonomer series **A** containing disecondary amino end groups:



$$CH_2{=}\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-OCH_2\underset{OH}{C}HCH_2-\left[R'-CH_2\underset{OH}{C}HCH_2-\overset{R}{N}-CH_2\underset{OH}{C}HCH_2\right]_n-R'-CH_2\underset{OH}{C}HCH_2\overset{R}{N}H$$

A

A$_0$: n=0
A$_1$: n=1
A$_2$: n=2 etc.

Also the concentration of these macromonomers **A** are relatively low w_0=0,016 (A_0 in Fig. 1), w_1=0,046 (A_1) and w_2=0,007 (A_2). In NMR spectra, the typical ^{13}C signal of the secondary amino end group $\underline{CH_2}NHR$ is observed at δ=46,7ppm.

The measured values w_x (HPLC) of macromonomers **M$_0$**, **M$_1$**, **M$_2$**, **M$_3$** etc. in a mixture of **M** differ from the expected weight fractions w_x[14,15] shown in table 3. These differences results because three macromonomer serieses **M**, **A** and **G** were formed which must calculated also.

Table 3 Mol-(n_x) and weight fractions (w_x) of **M-c** calculated[15,16] and measured by HPLC

	n_x(calc.)	w_x(calc.)	w_x(HPLC)	w_x(HPLC)	w_x(HPLC)
			M	**A**	**G**
n=0	0,167	0,220	0,199	0,055	0,016
n=1	0,250	0,250	0,239	0,046	0,024
n=2	0,208	0,195	0,168	0,020	0,005
n=3	0,146	0,132	0,086	0,007	0,002
n=4	0,094	0,084	0,044	-	-
n=5	0,057	0,051	0,019	-	-

In the IR spectrum of the macromonomers absorptions at 1640cm^{-1} of the olefinic double bond, at 1730 cm^{-1} of the ester carbonyl and in the region between 3200 and 3600 cm^{-1} with a maximum at 3480 cm^{-1} the hydroxyl groups are observed. Epoxy groups at 915

cm^{-1} and carboxylic acids at 1770cm^{-1} are not found.
Especially, in the ^{1}H-NMR spectra the signals of olefinic protons δ=5,45/6,05 ppm can be used for quantitative estimation of the functional end groups.

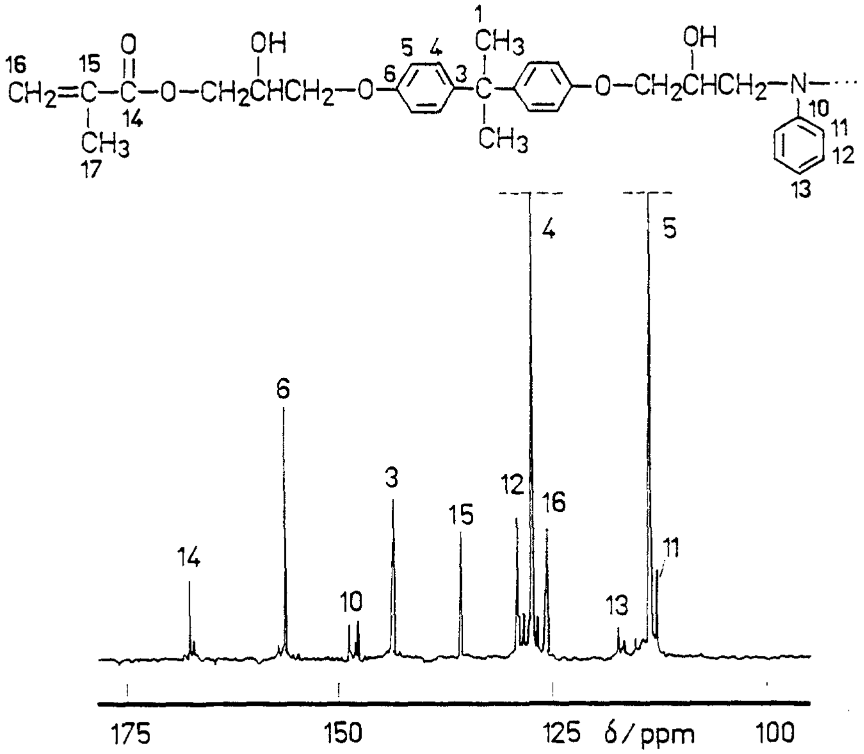


Fig.2 ^{13}C NMR-spectra of macromonomer **M-c** in $CDCl_3$

In the ^{13}C-NMR spectrum of the macromonomer **M-c** (fig 2.), signals of the methacrylic ester are to be seen at δ=167,4ppm (14), 135,9ppm (15), 126,1ppm (16), and 18,2ppm (17) as well as the signals of the bisphenol-A and aniline residue.
In not any case their are C-atoms of unreacted epoxy groups at 44, 50 and 68 ppm provable.

The photochemical polymerization of the macromonomers results in hybrid networks characterized by network segments of epoxide-amine units connected by poly(methacrylic ester) linkages. Their glass transition temperatures are relativly low, between 20 and 60 °C. The shrinking during the polymerization of macromonomers is expected to be low, 2 vol-% (**M-a**) and 1,4 vol-% (**M-d**).
Summarizing it can be stated that the described methacryloyl terminated epoxide-amine oligomers represent an interessting new typ of macromonomers, which may be used as both flexible and low-tension adhesives.

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Accepted October 28, 1991 C