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High-molecular weight diepoxide-dicarboxylic acid addition polymers

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SUMMARY

The addition polymerization of 2,2-bis[4-(2,3-epoxypropoxy)phenyl] propane (DGEBA) and dicarboxylic acid results in high molecular weight addition polymers (M_n 8000 - 13000). Their molecular weight distribution is rather broad (M_w/M_n=11,6) due to side reactions such as transesterification and formation of ether linkages. Due to the incorporation of the aliphatic dicarboxylic acid moieties in the polymer backbone, the addition polymers show relatively low glass transition temperatures ranging from 26 to 45 °C.

1. INTRODUCTION

For decades the polymerization of di- and polyepoxides and dicarboxylic acid anhydrides has played an important roll for technical applications such as cast resins, laminates, composites, and for surface protection (1-3). In contrast the polymerization of diepoxides and dicarboxylic acids received only slight attention due to the relatively slow addition polymerization and the necessity of high mixing temperatures and high reaction temperatures. Obviously, these high temperatures lead to non-definite networks. Furthermore, only network polymers obtainable from polycarboxylic acids and di- or polyepoxides result in materials with sufficient mechanical stability.

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Only low molecular-weight diepoxide-dicarboxylic acid adducts found an interest for modification reactions (4-6).

Serra et al (7) obtained soluble epoxide polyesterimides by reaction of diimid dicarboxylic acids and diglycidyl esters.

Fedtke (8) reported about the bulk addition polymerization of adipic acid and sebacic acid and DGEBA in the presence of dimethylaniline obtaining rather low molecular weight soluble oligomers having molecular masses of 1450 g/mol. In cyclohexanon solution molecular weights of M_n = 6600 g/mol were observed. However, always a higher consumption of epoxides was observed due to side reactions.

Recently, we have shown that the addition polymerization of diepoxides, dicarboxylic acids and monocarboxylic acids leads to new macromonomers (9). In order to setting the question if high molecular weight polymers are obtainable when diepoxides and dicarboxylic acids are being used we were interested in investigating this addition polymerization. Furthermore, the properties of the addition polymers and possible side reactions should be studied.

2. EXPERIMENTAL PART

Synthesis of additions polymers AP-1 to AP-3

AP-1: 6,808 g (20,00 mmol) of recrystallized DGEBA, 0,091 g (0,40 mmol) of triethylbenzyl ammoniumchloride (TEBAC) and 2,923 g of (20,00 mmol) adipic acid were homogeneously mixed for five to ten minutes at 140-150 °C. The obtained clear reaction mixture was deposited into six small vessels and reacted up to 32 hours at 90 °C (Table 1). Immediately after homogenization of the reaction mixture at 130-150 °C **AP-1a** was removed. The samples **AP-1b** to **AP-1f** were polymerized for 1½, 4, 8, 16 and 32 hours. **AP-1a** to **AP-1d** are soluble in dioxane and dimethylformamide whereas **AP-1e** and **AP-1f** are insoluble in these solvents.

AP-1d: $(C_{27}H_{34}O_8)_n$ M_n = 7780 g/mol, T_g = 45 °C.

AP-2: 6,808 g (20,00 mmol) of recrystallized DGEBA, 0,091 g (0,40 mmol) of TEBAC and 4,045 g (20,00 mmol) of sebacic acid were homogeneously mixed for five to ten minutes at 140-150 °C. The obtained clear reaction mixture was deposited into six small vessels and reacted to 32 hours at 90 °C up (Table 1). **AP-2a** to **AP-2c** are soluble in chloroform, dioxane and dimethylformamide whereas **AP-2d** to **AP-2f** are insoluble in these solvents.

AP-2c: $(C_{31}H_{42}O_8)_n$ M_n = 9500 g/mol, T_g = 32 °C

AP-3: 6,808g (20,00 mmol) of recrystallized DGEBA, 0,091 g (0,40 mmol) of TEBAC and 4,606 g (20,00 mmol) of dodecylic acid were homogeneously mixed for five to ten minutes at 140-150 °C. The obtained clear reaction mixture was deposited into six small vessels and reacted up to 32 hours at 90 °C (Table 1). **AP-3a** to **AP-3e** are soluble in chloroform and dimethylformamide.

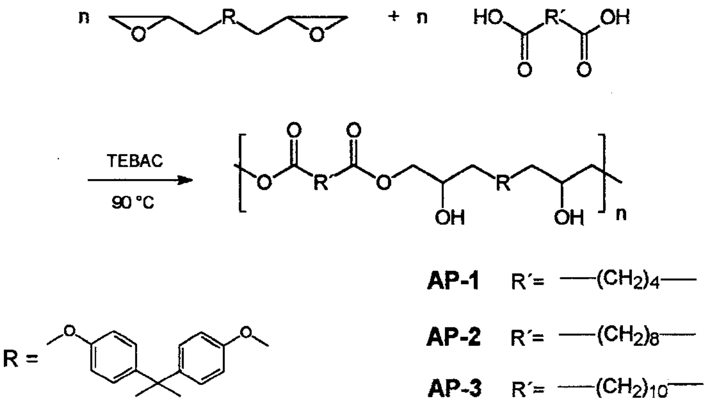
AP-3d: $(C_{33}H_{46}O_8)_n$ M_n = 12800 g/mol, T_g = 26 °C

Measurements

The molecular weights were estimated in chloroform, dioxane or dimethylformamide by using a vapor pressure osmometer (Knauer, Berlin). The IR-spectra were measured as film or in KBr by using a Specord M-80 (Carl-Zeiss, Jena). The ^{13}C NMR spectra were obtained in $CDCl_3$ with a 200 MHz apparatus (Bruker AC 200 and Bruker WP 200 SY). The glass transition temperatures were measured by using a DSC-2b (Perkin-Elmer). The investigation of the mol weight distribution of addition polymers was carried out with an apparatus (Knauer, Berlin) in tetrahydrofuran.

3. RESULTS AND DISCUSSION

As shown in *Scheme 1*, the addition polymerization of DGEBA and dicarboxylic acids such as adipic acid, sebacic acid and dodecyl acids leads to high molecular weight addition polymers **AP-1** to **AP-3** (10).



Scheme 1

Table 1 Molecular weights of addition polymers **AP-1 to AP 3** depending on the polymerization time, measured in chloroform at 37 °C

		AP-1	AP-2	AP-3
Sample	Reaction temp. (h)	M_n(vpo) (g/mol)	M_n(vpo) (g/mol)	M_n(vpo) (g/mol)
a	0 [a)]	-	-	4500
b	1,5	-	-	6200
c	4,0	7000 [b)]	9500	8600
d	8,0	7780 [c)]	cross linked	12800
e	16,0	cross linked	cross linked	13000
f	32,0	cross linked	cross linked	cross linked

a) Immediately after homogenization at 130-150 °C, b) M_n(vpo) in Dioxane, c) M_n(vpo) in DMF.

The molecular weights of addition polymers **AP-1 to AP 3** were estimated ranging from 7780 to 13000 g/mol. After eight hours a molecular weight of 13000 g/mol was found, which does not increase when the polymer is being heated further (Fig. 1). An increase of reaction time does not lead to polymers with higher molecular weight. Obviously, longer reaction times lead to side reactions and the addition polymers became insoluble.

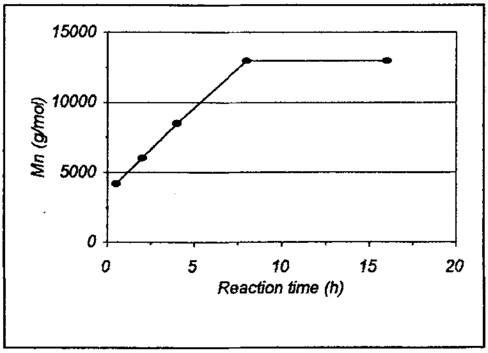


Fig. 1: Molecular masses of **AP-1c** depending on the reaction time

Depending on the length of the aliphatic groups in the dicarboxylic ester, the glass transition temperatures Tg of the addition polymers range from 26 °C (**AP-3d**) and 32 °C (**AP-2d**) to 45 °C (**AP-1d**).

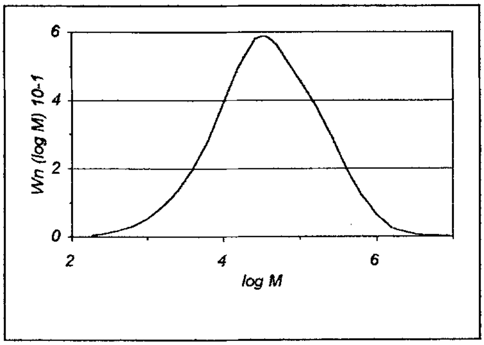


Fig. 2: Molecular weight distribution of polymer **AP-3d**

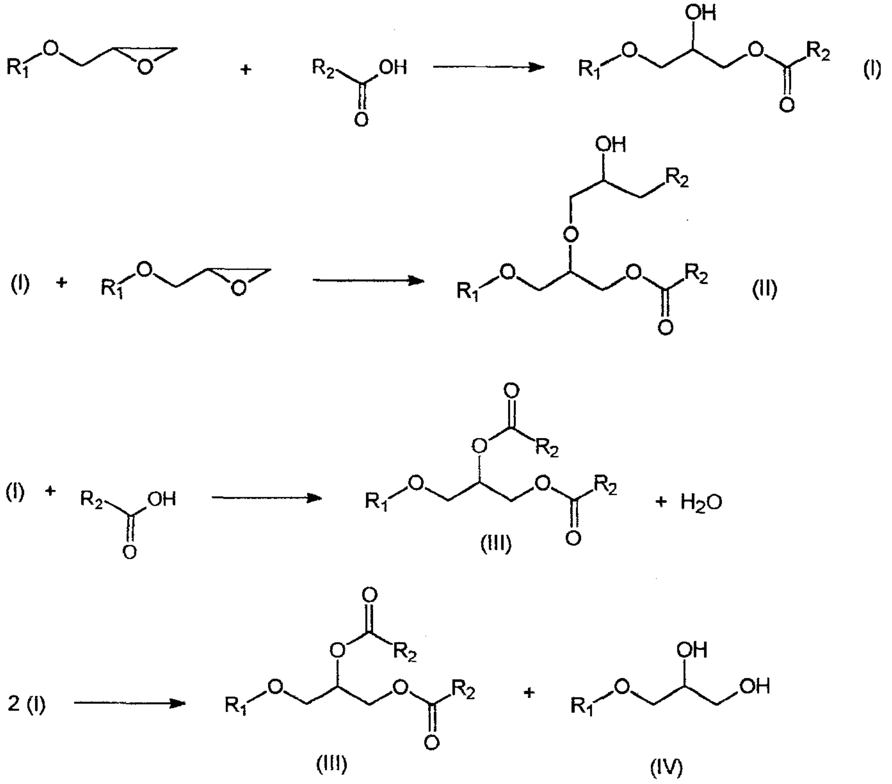
Tab. 2 Molecular weights of addition polymer **AP-3d**

Polymer	M_n (vpo) g/mol	M_n (GPC) g/mol	M_w (GPC) g/mol	M_z (GPC) g/mol	M_v (GPC) g/mol	M_w/M_n	α	lg k
AP-3d	12800	10000	117000	668000	58070	11,6	0,374	-2,113

By using size exclusion chromatography (SEC) the molecular weight distributions were estimated as well as parameters α and k of the Mark-Houwink equation. The molecular weight distribution of **AP-3d** (Fig. 2, Tab. 2) is relatively broad (M_w/M_n = 11,6). Usually, the formation of cyclic oligomers and side-branched polymers is supposed to be the reason of broader molecular weight distributions.

Dušek has shown that some following reactions and side reactions take place during the formation of epoxide-carboxylic acid networks such as ether formation, transesterification and condensation esterification (11-13) (*Scheme 2*).

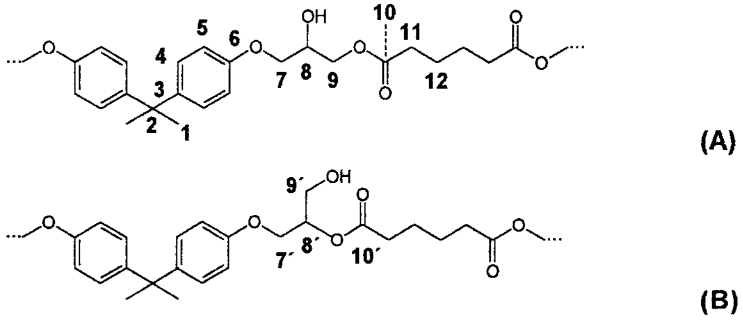
Fedtke et al (8) found a higher consumption of epoxide groups related to carboxylic acid groups at the addition polymerization of epoxides and carboxylic acids. The formation ether linkages should be responsible. By using ^{13}C-NMR investigations of the amine catalyzed reaction of dodecylic acid and phenyl glycidyl ether the formation of two isomers of the ring opening reaction was observed and exclusively transesterification reactions (14).



Scheme 2

Due to an exchange of the mechanism of the addition polymerization between S_N1 and S_N2 in the polymers isomers **(A)** and **(B)** are provable. In the ^{13}C-NMR spectrum (Fig. 3) the isomer **(B)** appear by signals of C-7′ (66,2 ppm), C-8′ (72,9 ppm), C-9′ (61,8 ppm) and signals of the sp^2-hybridised C-10′ (173,1 ppm), (Tab. 3, Fig. 3).

Further side products of **AP-1** are not provable by using the ^{13}C-NMR spectrum (Fig. 3). On the other hand the high value M_W/M_n = 11,6 of **AP-3** and the cross linking of **AP-1** to **AP-3** after long reaction times indicate that side-branching reactions occur.



Scheme 3

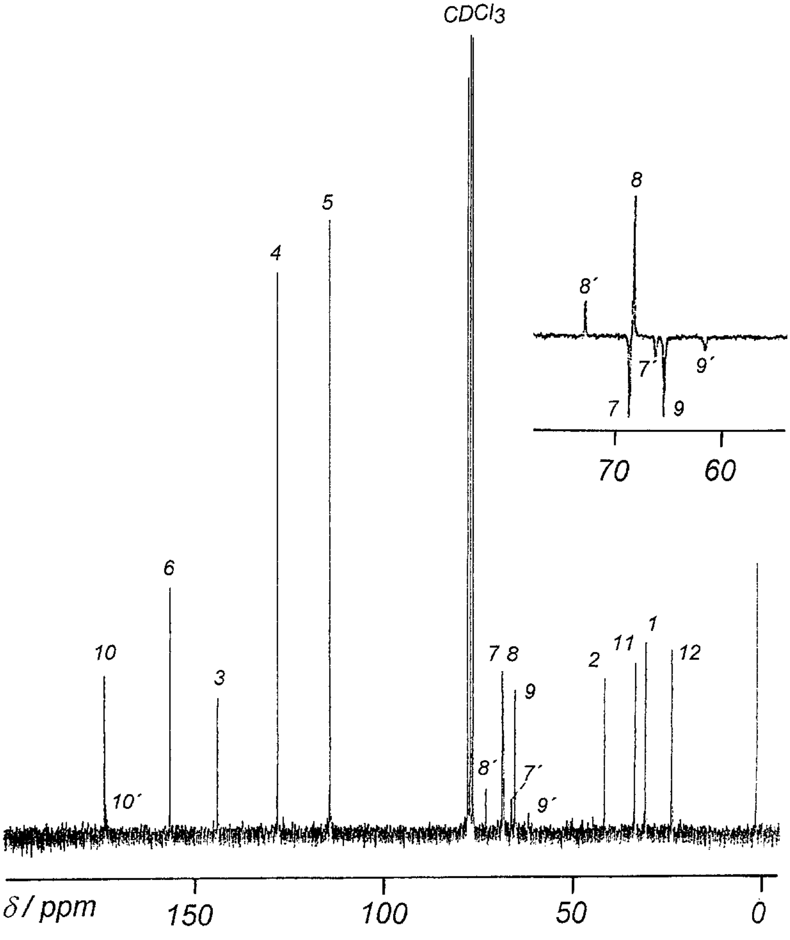


Fig. 3 ^{13}C-NMR spectrum of **AP-1** in $CDCl_3$

Tab. 3 ^{13}C-NMR Spectrum of **AP-1**

C-atom	δ/ ppm	C-atom	δ/ ppm
1	30,9	8	68,4
2	41,6	8′	72,9
3	143,7	9	65,4
4	127,8	9′	61,8
5	113,9	10	173,4
6	156,1	10′	173,1
7	68,6	11	33,6
7′	66,2	12	24,1

CONCLUSION

In order to obtain high molecular weight addition polymers (M_n > 8000 g/mol) of DGEBA and aliphatic dicarboxylic acids suitable conditions must be fulfilled (reaction temperature of about 90 °C, reaction time six to eight hours). Due to an exchange of the mechanism of the addition polymerization between S_N1 and S_N2 in the obtained polymers isomeric structures **(A)** and **(B)** are provable. The obtained mol weight distribution lead to the conclusion that further side reactions take place.

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