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Azo polymers – syntheses and reactions

5. Azo group containing polycarbonates – synthesis, characterization and initiator properties

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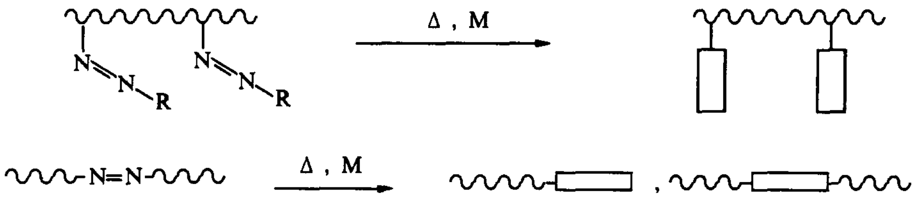
Summary

Polycarbonates containing different amounts of thermolabile azo functions have been synthesized. The resulting polymeric initiators have been used to start the polymerization of methyl methacrylate. The kinetic results are explained on the basis of a high degree of termination reactions by primary radicals.

Introduction

Polymers containing azo groups are of interest for the synthesis of graft- and blockcopolymers[1].



The combination of condensation type polymers with those synthesized by polymerization are particular interesting, since most of those physical combinations are not compatible. One way to solve this problem would be their chemical linkage by grafting polycondensate with polymerizates[2]-[4]. This chemical linkage can be realized by using of polymeric initiators such as polycarbonates containing azo functions, for the polymerization of common monomers[3],[4]. Although, the potential of this reaction has been demonstrated already, more detailed studies were necessary in order to understand the consequences of the application of polymeric instead of low molar mass initiators for the polymerizations.

Polycondensation

The reaction of bisphenol A® and phosgene in the presence of pyridine at room temperature yields polycarconates with molar masses up to 70 000.
($\overline{M}_{APC}$, calibrated by polycarbonate standards**)
In model studies, in which this polycondensation was carried out in the presence of azo compound 1 a remarkable retarding effect of the azo compound on the molar masses was observed (Fig. 1).

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** We wish to thank Dr. A. Horbach, BAYER AG Krefeld, for these standards

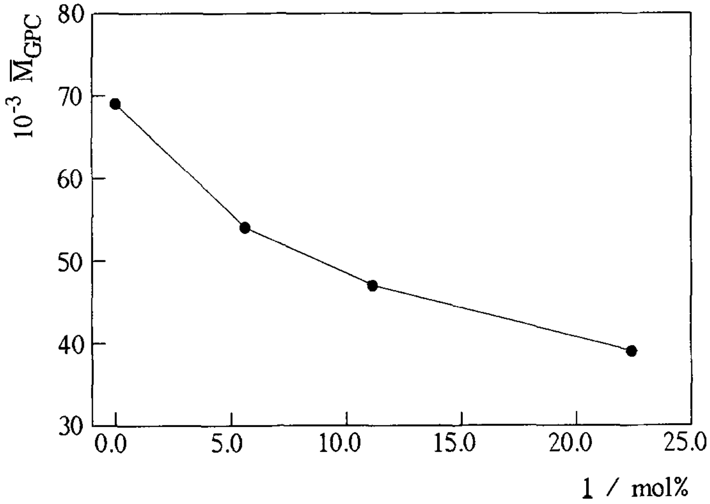
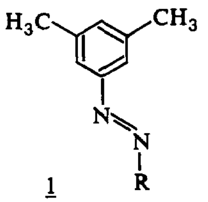
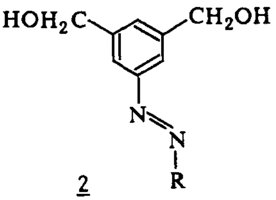


Fig. 1: Retardation of the molar mass of polycarbonate by azo compound 1



1



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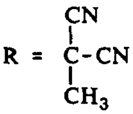

$$R = C(CN)_2CH_3$$

This retardation was even stronger when cocondensation experiments with 2 were carried out (Table 1).

Table 1: Molar masses of the azo-polycarbonates (APC)

APC	molar masses GPC($\overline{M}_n$)	 VPO($\overline{M}_n$)	$\overline{M}_w / \overline{M}_n$
1	15900	5400	2.94
2	13300	7800	1.70
3	13300	8000	1.66
4	10200	5100	2.00

The content of azo functions in the polymer was varied between 4 and 20 mol % (Table 2).

Table 2: Azo content of the APC's

		mol % azo in polymer				
APC	mol % 2 in monomer	UV	DSC	elemental analysis		$\overline{azo}$
1	5	4.0	4.4	4.3[a)]	4.2[b)]	4.2
2	16.5	14.7	14.2	14.9	13.7	14.4
3	21.9	19.3	19.1	19.5	19.3	19.3
4	21.8	19.6	19.8	19.5	19.6	19.6
5	9.9	8.9	8.9	9.3	9.3	9.1

a, b, elemental analysis was carried out from two different commercial instituts.

The azo content was determined by UV-spectroscopy, by DSC and elemental analysis. The values received from elemental analysis and DSC (calibrated with the decomposition enthalpy of the corresponding model compound 1, $\Delta H_{decomp} = 184$ KJ mol^{-1}) show good agreement. Very accurate values were received from UV-measurements in which the spectrum with the highest azo content (sample 4) was calibrated with its elemental analysis. It's also possible in principle to determine the azo content by ^1H-NMR spectroscopy - however the results received by comparison of the CH_2-O-group of 2 with the aromatic protons show greater scattering.

The average number of azo functions per chain (F) was calculated from the number degree of polymerization and the azo content of the polycarbonate (Table 3).

Table 3: $\overline{DP_n}$ and average number of azo functions per polymer chain (F)

APC	$\overline{DP_n}$	F
1	21	0.9
2	31	4.5
3	31	6.0
4	20	3.9
5	20	1.8

APC as Initiator

Decomposition rate

The kinetics of the monomeric and polymeric azo compounds were studied by DSC[5)].

The advantages of this method compared to others are 1) very small samples are needed only 2) from one run a great number of kinetic data are available.

However, it is essential to control the kinetic result, received from DSC by an other method or to know that no secondary reaction take place beside the decomposition of the azo function. This is indeed fulfilled for a great number of symmetrical and unsymmetrical azo compounds[6)-10)].

The decomposition kinetics is of first order for the monomeric and polymeric azo compound. Moreover, the kinetic data are almost identical when the decomposition was studied in solution. The solvent-free decomposition of the azo polycarbonate is remarkably slower than that in solution (Table 4).

Table 4: Kinetic Data received from DSC

azo compound	10^5 k/s^{-1} 60°C	 70°C	 80°C	E_A/KJ mol^{-1}
2[1]	0.17	0.74	2.98	142
APC 2[1]	0.12	0.53	2.02	137
APC 2[2]	0.02	0.08	0.35	154

1) in phthalic acid dibutyl ester
2) in substance

The difference between the results in solventcontaining and solventfree system is not surprising, since it was known from earlier investigations that the increasing viscosity of the system yields a decrease of the overall rate constants[6)-8)]. This phenomena was explained by the cage effect and higher rate of the back reaction to the original compound of the primary formed radicals

$$[R^1\text{-N} = \text{N-}R^2]_{cage} \rightleftharpoons [R^1\cdot + \cdot\text{N} = \text{N-}R^2]_{cage}$$

$$R^1\cdot_{free} + \cdot\text{N} = \text{N-}R^2_{free}$$

$$\cdot R^2_{free} + N_2\ .$$

Polymerization of MMA, initiated by APC

The polymerization of MMA was carried out in 1.4-dioxane as a solvent at 80°C. In order to determine the rate of the reaction and its dependence from [M] and [I] both the concentration of the monomer and of the initiator was varied systematically. The polimerization rate v_{br} was determined by dilatometry. The results are shown in Fig. 2 and Fig. 3.

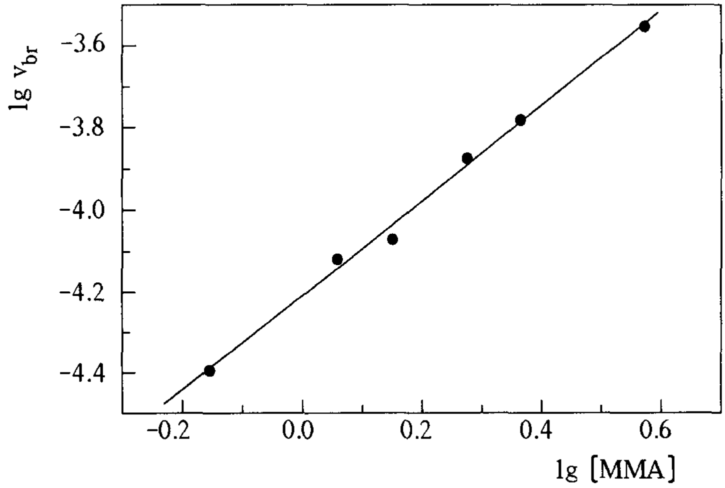

Fig. 2: Polymerization of MMA initiated by APC; v_{br} = f[M]

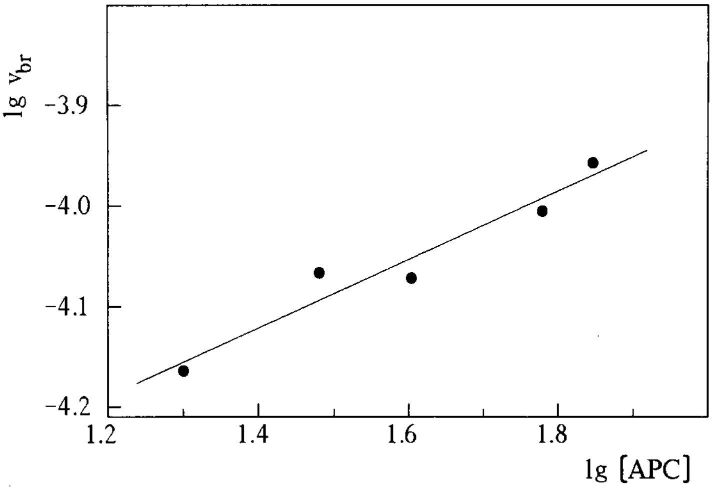

Fig. 3: Polymerization of MMA initiated by APC; v_{br} = f[M]

The variation of [I] was realized by using different amounts of APC with a certain amount of azo function but also by using a certain amount of APC containing different amounts of azo. In all cases the results were similar (Table 5).

Table 5: Exponents of the kinetic equation $v_{br} = k[M]^m[I]^n$

APC	mol % Azo	m	n
1	4.2	1.16	0.34
2	14.4	1.16	0.35
3	19.3	1.19	0.34
5	9.1	1.17	0.34

Such deviations from the commonly found m = 1 and n = 0.5 can be explained on the basis of a high degree of termination by primary radicals[11)-14)]. Such termination is also discussed in connection with the Trommsdorff-effect in which the normal termination by polymeric radicals becomes more and more hindered due to the increasing viscosity of the system. In contrast to polymeric radicals the small primary radicals are still mobil enough and therefore termination by those radicals becomes increasingly important. An early Trommsdorff-effect is quite likely in polymerization processes described here due to the fact that these systems already contain 2 - 7 weight % polymer at $t = t_o$.

Experimental part

Azo compounds

((3,5 - dimethyl) phenyl azo) - methylmalonodinitrile (1)

15.45 ml (0.124 mole) of freshly distilled 3,5-dimethyl aniline was dissolved in 150 ml distilled water and 113 ml conc. HCl (32 %) and then cooled to 0°C. Then a solution of 9.31 g (0.135 mole) $NaNO_2$ in 55 ml distilled water was added dropwise converting the amine into a diazonium salt.

A solution of 9.92 g (0.124 mole) of methylmalonodinitrile in 150 ml ethanol and this diazonim salt solution were added dropwise from separated precooled dropping funnels into a solution of 234 g sodium acetate in 600 ml water.

The yellow precipitate was separated by filtration and recrystallized from petrolether/ethanol

m.p.: 49°C
yield: 89 %
elemental analysis $C_{12}H_{12}N_4$ (212,3)
N(calc. 26.40 %, exp. 26.47 %)
UV(C_2H_5OH): λ_{max} = 293 mm, (lgε = 4.08)
IR(KBr): 2250 cm^{-1} (CN), 855 cm^{-1}, 685 cm^{-1}: 1, 3, 5-trisubstituted aromat
^1H-NMR ($(CD_3)_2CO$) δ(ppm) (rel. to TMS)
2.24 3H, s(CH_3);
2.40 6H, s(CH_3);
7.28 (1H, s aromatic H);
7.46 (2H, s aromatic H);

3,5-Di(hydroxymethyl)phenylazo-methylmalonodinitrile

3-hydroxymethyl-5-nitrobenzylalcohol was reduced to the corresponding amine by reduction with zink dust according to a discribtion in the literature[62)]. This amine was converted into 2 analogous to the description given for 1.

m.p. 118°C
yield 94 %
elemental analysis $C_{12}H_{12}D_2N_4$ (244,3)
N(calc. 22.94 %, exp. 22.76 %)
UV(C_2H_5OH): λ_{max} = 290 mm, (lgε = 4.06)
IR(KBr): 2250 cm^{-1} (CN)
1, 3, 5-trisubst. aromat: 865, 695 cm^{-1}
^1H-NMR($(CD_3)_2CO$), δ(ppm): 2.25 (2H, s(OH)
2.27 (3H, s(CH_3))
4.75 (4H, s(CH_2-O)
7.61, 7.73 (3H, 2×s, aromatic H)
^{13}C-NMR($(CD_3)_2CO$), δ(ppm): 24.8 (methyl-C); 64.0 (methylen-C);
64.4 (quart. C); 111.0 (C≡N); 120.7; 130.5; 145.5;
151.2 (aromatic C).

Cocondensation

A typical cocondensation was carried out in a 1 l SOVIREL® reactor equipped with condensor of stirrer which was flushed with dry nitrogen. 1.1 g ($4.5 \cdot 10^{-3}$ mole) 2 and 19.5 g ($85.5 \cdot 10^{-3}$ mole) were dissolved in 235 ml of pyridine. Then the calculated stoichiometric amount of phosgene was added in a period of 40 min. Further addition of $COCl_2$ was carried out in small portions. The end of reaction is indicated by a sharp increase of viscosity. Then the mixture was diluted with chloroform, until a clear green solution was observed. This solution was dropped into a eight- to tenfold amount of methanol. The precipitate was cleaned by two reprecipitation cycles from chloroform/methanol.

Polymerization kinetics

Methyl methacrylate was cleaned as described in the literature[16)].
The kinetics was followed by dilatometer.
The conversion was controlled by gravimetry.

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