

Azo polymers – syntheses and reactions

6. Grafting of polycarbonates

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Summary

Azo group containing polycarbonates were used as initiators for the polymerization of methyl methacrylate. The grafting reaction was characterized by the terms: grafting success U_g , grafting efficiency ε and degree of grafting π . The effect of the monomer and initiator concentration on these terms is discussed in detail. The number of grafted sidearms is determined by complete hydrolysis of the polycarbonate backbone.

1. General Considerations

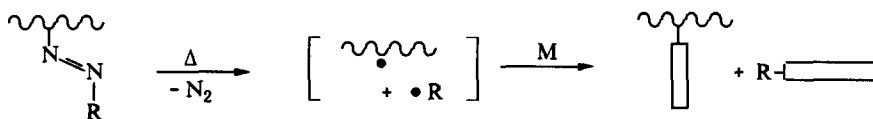
Grafting reactions can be characterized by terms first defined by J.P. Fischer¹⁾:

$$\text{Success of grafting } U_g [\%] = \frac{\text{grafted backbone}}{\text{grafted} + \text{ungrafted backbone}} \cdot 100 \%$$

$$\text{Grafting efficiency } \varepsilon [\%] = \frac{\text{sidearm polymer}}{\text{sidearm polymer} + \text{homopolymer}} \cdot 100 \%$$

$$\text{Degree of grafting } \pi [\%] = \frac{\text{sidearm polymer}}{\text{sidearm polymer} + \text{backbone}} \cdot 100 \%$$

$U_g = 100\%$ should be possible by using polymeric azo initiators with more than two azo initiator functions per chain. Usually ε -values are in the order of $\varepsilon < 50\%$. Higher values are observed if the two primary radicals show different reactivity towards monomer. Ideally, the polymeric radical P^\bullet should be active for polymerization and the low molar mass radical R^\bullet should be inactive^{2),3)}.

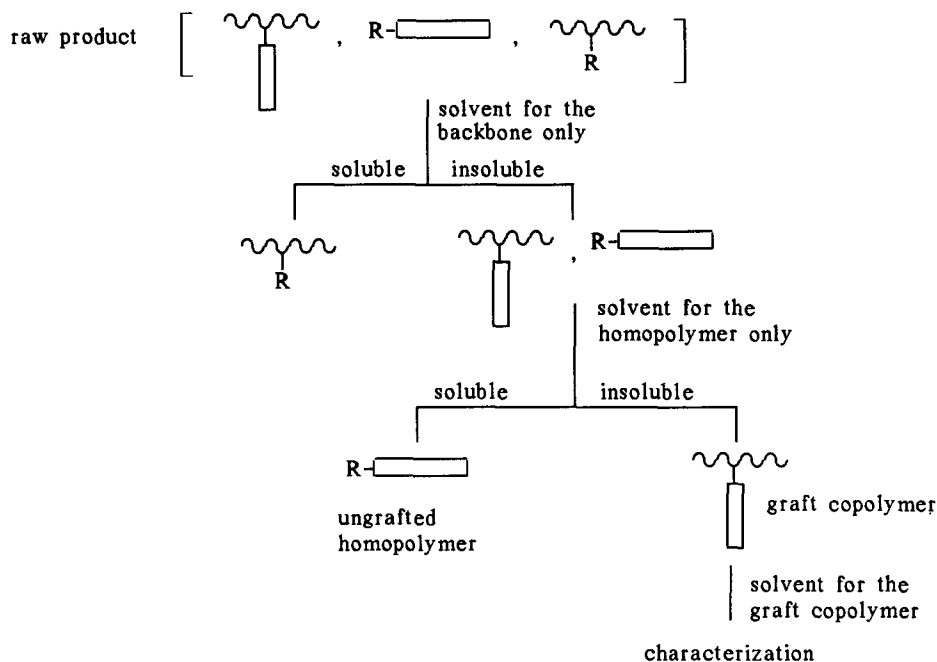


The degree of grafting π depends on

- 1) the ratio of monomer to initiator
- 2) number of azo functions per polymer chain
- 3) conversion of monomer and azo functions.

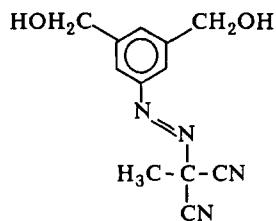
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The parameter π is more or less adjustable by the experimental conditions. In order to determine these terms the raw product has to be fractionated:



2. Grafting of Polycarbonate

Polymeric initiators composed of polycarbonate backbone and azo functions in the side chains were synthesized by cocondensation of bisphenol A[®] and **1** with phosgene has already been described⁴⁾:



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The following polymeric initiators were synthesized and characterized (Table 1).

Table 1: Polymeric initiators - starting material for the syntheses of graftcopolymers

APC	$\bar{a}z\bar{o}$ Mol %	\bar{M}_n a)	\bar{M}_w b)	F c)
1	4.3	5400	15900	0.9
2	14.4	7800	13300	4.5
3	19.3	8000	13300	6.0
4	19.6	5100	10200	3.9

- a) determined by vapor osmometry
 b) determined by GPC using polycarbonate standards
 c) average number of azo function per polymer chain, calculated on the basis of \bar{M}_n and $\bar{a}z\bar{o}$.

Application of APC 1 to APC 4 as initiators for the polymerization of methyl methacrylate yielded graftpolymers contaminated by homo-PMMA which was initiated by R^\bullet ($R^\bullet = \bullet C(CN)_2(CH_3)$). After quantitative fractionation of the raw product of grafting these reactions could be characterized by the three terms U_g , ϵ and π .

3. Results and Discussion

In all cases, except for APC 1, $U_g = 100\%$ was observed - meaning that all polycarbonates were converted into graftcopolymers. From Fig. 1 to Fig. 6 one can see that ϵ , π and the monomer conversion C increases with increasing $[M]$ (Fig. 1 - Fig. 3) but decreases with increasing initiator concentration $[APC]$ (Fig. 4 - Fig. 6).

The ϵ -values are generally higher than 50% - this result can be explained on the basis of the difference in reactivity of the primary radicals. The polymeric phenyl-radical is more reactive than the low molar mass radical $\bullet C(CN)_2(CH_3)$. The increase of ϵ with $[M]$ can be understood, when one assumes two areas of chain growth^{5),6)}.

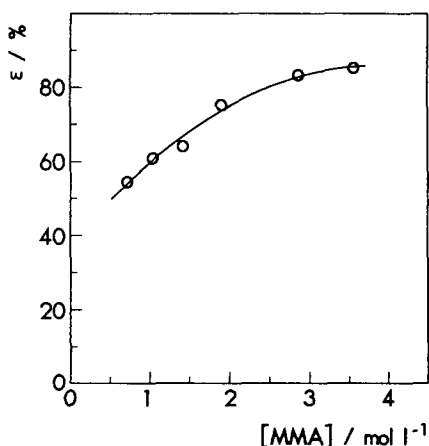


Fig. 1: $\epsilon = f([M])$,
at 80°C , $[APC1]_0 = 40.0 \text{ g l}^{-1}$

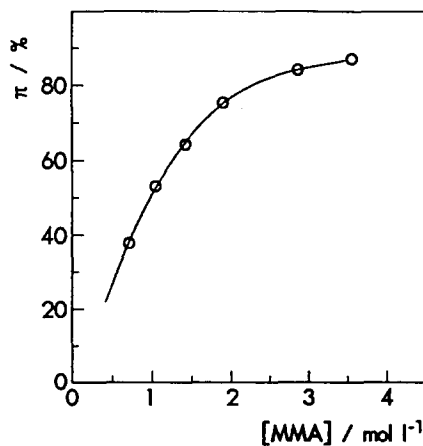


Fig. 2: $\pi = f([M])$,
at 80°C , $[APC2]_0 = 40.0 \text{ g l}^{-1}$

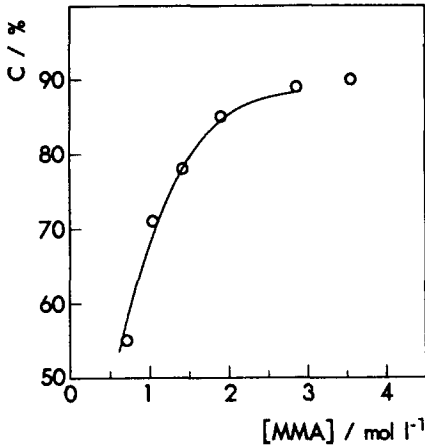


Fig. 3 : $C = f([M])$,
at 80°C, $[APC2]_0 = 40.0 \text{ g l}^{-1}$

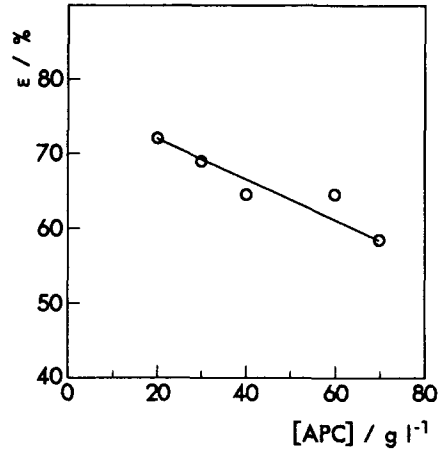


Fig. 4 : $\epsilon = f([APC])$,
at 80°C, $[MMA]_0 = 1.4 \text{ mol l}^{-1}$

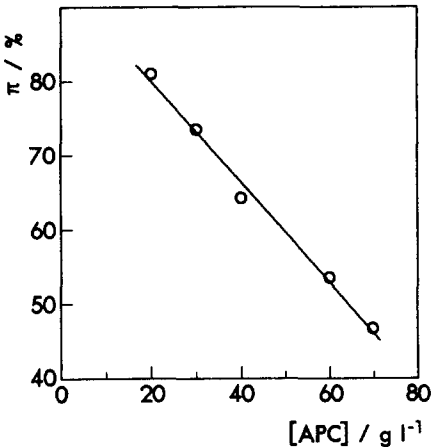


Fig. 5 : $\pi = f([APC])$,
at 80°C, $[MMA]_0 = 1.4 \text{ mol l}^{-1}$

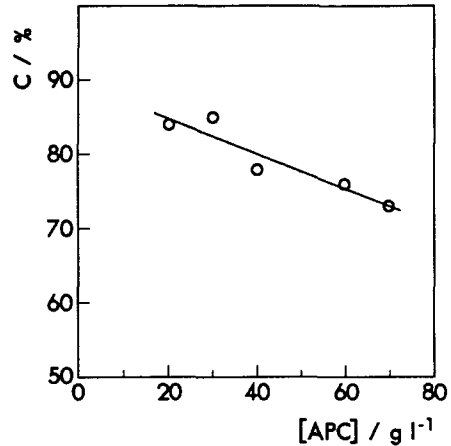


Fig. 6 : $C = f([APC])$,
at 80°C, $[MMA]_0 = 1.4 \text{ mol l}^{-1}$

- 1) The polycarbonate coil with high viscosity where the polymerization is controlled by an early Trommsdorff-effect.
- 2) Polymerization outside the polycarbonate coil, which is started by $\cdot C(CN)_2(CH_3)$ - in this area the viscosity is lower than inside the coil, the Trommsdorff-effect can be neglected here or occurs later than inside the initiator coil.

This view is supported by the higher degree of polymerization for the side chains of the graftcopolymer compared to the simultaneously formed homo poly-MMA. (The molar masses of these side chains were determined after hydrolysis of the polymer backbone (Table 2)).

Table 2: Molar masses of the PMMA side chains compared to the simultaneous formed homo-PMMA as a function of the monomer concentration. Initiator: [APC 2] = 40.0 g l⁻¹; solvent: dioxane; T = 80°C, t = 24 h

[MMA] mol l ⁻¹	(PMMA) _g ^{a)}	(PMMA) _h ^{b)}
0.71	36 000	32 000
1.04	40 000	33 000
1.42	53 000	35 000
1.90	66 000	36 000
2.86	85 000	40 000
3.56	108 000	42 000

- a) molar masses of the side chains, determined after hydrolysis of the polycarbonate backbone
 b) molar masses of the homopolymer, initiated by R[•], both determined by GPC, using polystyrene standards

The increase of π with increasing [M] is in agreement with these results. Constant amount of APC and longer side chains must yield higher π -values by definition. The increase of the conversion with increasing [M] is explained by the glass effect⁷⁾⁻¹¹⁾. Following the interpretation of the glass effect, increased viscosity of the system and therefore decreased mobility of the monomer are responsible for uncomplete monomer conversions.

The glass effect is extended to higher conversions of M with increasing [M], due to a viscosity decrease and an increase of the APC-free area, meanwhile higher [APC] decreases the conversion at which the glass effect occurs.

More polymeric initiator means a higher macroscopic viscosity or using the "two-phase-reactor"-picture the area of polymeric coil increases and therefore the area showing an early glass effect increases. Thus, the conversion of monomer decreases. Since the molar mass of the homopolymer does not change with the amount of polymeric initiator one can conclude that the [M]/[R[•]] ratio does not change in this phase (Table 3).

Table 3: Molar masses of the PMMA side chains compared to the simultaneous formed homo-PMMA as a function of [APC]

APC 2 g l ⁻¹	(PMMA) _g ^{a)}	(PMMA) _h ^{b)}
20.1	67 000	35 000
30.1	59 000	34 000
40.0	53 000	35 000
59.9	43 000	34 000
69.8	40 000	33 000

- a) molar masses of the side chains, determined after hydrolysis
 b) molar masses of the homopolymer, initiated by R[•] both determined by GPC, using polystyrene standards

An alternative way to increase the initiator concentration is to use a polymeric initiator with a higher content of azo functions. The two-phase-reactor model can again be used to explain the experimental results: The side chain become shorter with increasing $[I]$ inside the coil. This dependence is known from common polymerizations. Increasing viscosity, due to the greater number of growing chains in a constant volume means an earlier glass effect and therefore lower conversion of $[M]$. In addition termination by primary radicals becomes increasingly important.

Outside the coil the ratio $[M]:[R^*]$ seems to be balanced by the higher overall $[R^*]$ but also by the increase of the termination with primary radicals, since no change of the molecular weight of the homopolymer was observed in these experiments.

The two-phase-model can also explain the decrease of ϵ with increasing APC. Since side chains become shorter with increasing APC and homopolymer do not change their molar masses with respect to APC, ϵ -values must decrease. The same argument holds for π - higher APC concentration means shorter chains and therefore smaller π .

4. Number of Side Chains

Usually the grafting reactions were carried out at 80°C . Due to the glass effect the conversion of monomer stops before the monomer is consumed completely. In general, this happens after less than one half life time of the initiator.

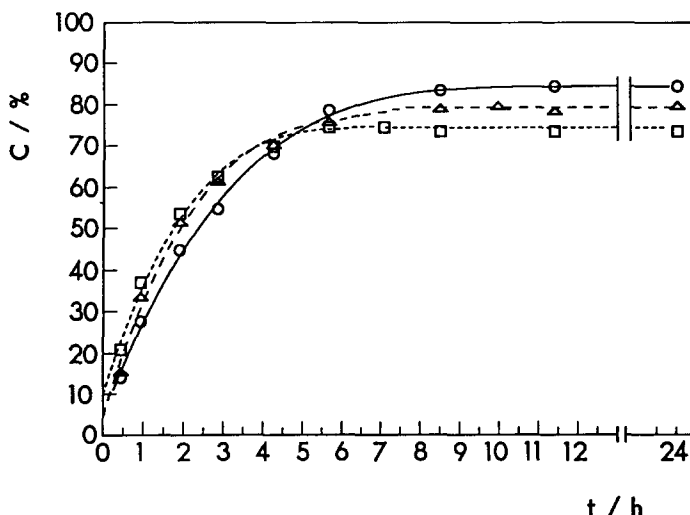


Fig. 7: time conversion curve for MMA initiated by APC at 80°C : $[M]_0 = 1.4 \text{ mol l}^{-1}$,
 \circ $[\text{APC}]_0 = 20 \text{ g l}^{-1}$, Δ $[\text{APC}]_0 = 40 \text{ g l}^{-1}$, \square $[\text{APC}]_0 = 60 \text{ g l}^{-1}$.

That means that at longer reaction time more than 50% of the azo group decompose without any effect to the grafting. Therefore it is not surprising that the average number of side arms per polymer was determined to be $n \cong 1$ in all cases independent of the functionality of the polymeric initiators (Table 4).

In order to increase the average number of side chains the reaction temperature was increased from 80°C to 170°C . This grafting reaction was carried out in an autoclave. By this temperature increase it was possible to raise the number of sidearms from 1 to 2.7.

Table 4: Grafting results at 80°C and at 170°C
 average molar masses of the initiators ^{a)}, graftcopolymers ^{b)}
 grafted sidearms ^{b)} and the average number of sidearms n

T °C	I Initiator	II Graftcopolymer	III sidearms	II - I	$\frac{II - I}{III} = n$
80	APC 1	127 000	110 000	111 000	1
	$\bar{M}_{GPC} = 15900$	107 000	94 000	91 000	1
	F = 0.9	98 000	87 000	92 000	1
80	APC 2	73 000	59 000	60 000	1
	$\bar{M}_{GPC} = 13300$	64 000	53 000	51 000	1
	F = 4.5	52 000	40 000	39 000	1
80	APC 3	50 000	39 000	38 000	1
	$\bar{M}_{GPC} = 13300$	43 000	37 000	30 000	0.8
	F = 6	79 000	60 000	66 000	1.1
170	APC 2	137 000	45 000	124 000	2.7

a) determined by GPC using polycarbonate standards

b) determined by GPC using polystyrene standards

Experimental Part

Syntheses

The Azo group containing polycarbonates (APC) were synthesized as already described ⁴⁾.

Graftcopolymers

The APC and MMA were dissolved in dioxane. The grafting reaction was carried out in a Schlenck reactor at 80°C and in an autoclave at 170°C respectively. The conversion was followed gravimetrically. After 24 h the polymerization was stopped. The raw product was isolated by precipitation into methanol.

Fractionation

1 g of the raw graftcopolymer was dissolved in 15 ml dioxane. The first fraction was received by precipitation into a solution of 41 ml dioxane and 124 ml methanol (with 2 drops of conc. HCl added). The graftcopolymer was isolated by filtration, the homopolymer (PMMA) was received by collecting the filtrate and evaporation of the solvent. Both fractions were free of ungrafted polycarbonate, which was proved by GPC:

a) The graftcopolymer is unimodal and does not show a signal in the region of APC.

b) The PMMA fraction is free of UV-absorption.

Hydrolysis

0.3 - 0.4 g of the graftcopolymer were dissolved in 10 ml dioxane. Then 10 ml of conc. NH_3 -solution were added. This mixture was stirred for 30 h at 50°C. The resulting product was isolated by precipitation into methanol.

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