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SYNTHESIS AND CHARACTERISATION OF SOME NEW THERMOGRAFTED POLYCARBONATES

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ABSTRACT

Several synthetic copolymers of bisphenol-A (I) and 1,1,1-trichloro-2,2-bis(4-hydroxyphenyl)ethane (II) were synthesised and characterised. Acrylonitrile monomer was then grafted onto the copolymer (5% **II** and 95% I) thermochemically using $Mn_2(CO)_{10}$ as thermoinitiator. Different degrees of grafted copolymers were synthesised and characterised. The effects of three factors on the average degree of grafting were examined: polymerisation temperature; polymerisation time; and monomer concentration.

INTRODUCTION

In a previous study [1], a new type of copolycarbonates of bisphenol-A (**I**) and 1,1,1-trichloro-2,2-bis(4-hydroxyphenyl)ethane (**II**) containing different molar ratios of **II** were synthesised and acrylonitrile monomer was grafted onto these copolymers photochemically [2]. For the present study it was decided to graft acrylonitrile onto the above copolymer by a thermochemical reaction using $Mn_2(CO)_{10}$. Similar reactions have been previously described by Bamford et al. as initiating systems using $Mo(CO)_6$ at 80 °C [3]. The factors affecting the average degree of grafting were also examined.

EXPERIMENTAL

Materials

The copolycarbonates of **I** and **II** containing 4.9% of comonomer **II** were synthesised and characterised according to ref. 1.

Acrylonitrile was supplied by BDH and dimethylformamide (DMF) was supplied by Fluka. Both were purified by fractional vacuum distillation.

$Mn_2(CO)_{10}$ was supplied by Fluka and purified by sublimation under reduced pressure (0.1 mm Hg). The other reagents and solvents were used as supplied.

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Polymerisation procedure

The reaction vessel was charged with acrylonitrile, $Mn_2(CO)_{10}$ (10^{-4} mol), DMF (30 ml) and 4.9% copolymer (10^{-2} mol), and flushed with dry pure nitrogen for 30 min. The reaction vessels were sealed and placed in a shaking oil bath at the desired temperature. The grafting reactions were studied as a function of temperature, acrylonitrile concentration and reaction time.

Purification of the grafted copolymers

The reaction mixture was poured into a beaker containing 500 ml of distilled water. The crude polymer was filtered, washed with distilled water, and refluxed with 100 ml saturated KSCN solution to extract the homopolyacrylonitrile [5]. Finally, the grafted copolymers were dissolved in DMF and reprecipitated with distilled water, then dried under vacuum at 80°C for 48 h.

Characterisation of the grafted copolymers

Polymer analysis

The grafted copolymers were analysed by elemental analysis, IR and NMR spectroscopy. The analyses were carried out at the Alfre Bernhardt Mikroanalytisches Laboratorium, West Germany. The elemental analysis data for the grafted copolymers are given in Table 1.

Viscometry

The intrinsic viscosities of the grafted copolymers were measured at 25 ± 0.01°C using Ubbelohde suspended-level viscometers. These are also given in Table 1.

TABLE 1

The elemental analysis results (%) for the grafted copolymers

Sample No.	$[\eta]$ ($cm^3\ g^{-1}$)	C	H	Cl	N	Average degree of grafting, $\overline{X}_g$
1	58.5	74.26	5.72	2.42	—	(prepolymer)
2	60.3	73.34	5.58	1.54	0.71	2.7
3	63.5	72.50	5.26	1.28	2.88	12.1
4	63.8	71.63	5.67	0.81	3.45	14.8
5	107.2	70.04	5.48	0.77	13.58	104.0
6	140.3	71.81	5.80	0.82	18.07	212.7
7	144.2	66.84	5.80	0.78	19.12	256.9
8	155.0	66.27	5.73	0.79	20.09	369.7

The calculated values for 4.9% prepolymer were (%): C, 74.05; H, 5.32; Cl, 2.43.

Thermogravimetry

The thermogravimetric (TG) analyses were carried out on a MOM derivatograph thermoanalyser. All measurements were made in the presence of air and against standard α-Al_2O_3.

RESULTS AND DISCUSSION

The elemental analysis results shown in Table 1 confirm that the thermografting of acrylonitrile by thermochemical initiation is successful. Thus, %Cl decreases while there is a substantial increase in %N, which leads to different degrees of grafting (see Table 1, as calculated from the analysis data).

Other evidence confirming grafting is the drastic change in the intrinsic viscosity as a function of the degree of grafting. There is also spectroscopic evidence, i.e., an absorption band was observed at 2240 cm^{-1} due to the nitrile group vibration.

The TG curves for the grafted copolymers (Fig. 1) also confirm the occurrence of grafting. The decomposition process takes place in two stages: the first stage (260 °C) shows the loss of HCN from the grafted portions; the final decomposition is seen at > 550 °C. The complete thermal and mechanical characteristics of these new copolymers are to be published soon [6].

By studying the effect of the grafting temperature on the average degree of grafting (Table 2) it was found that it reaches an optimum at ca. 80 °C. This is probably the most convenient temperature for the decomposition of the catalyst.

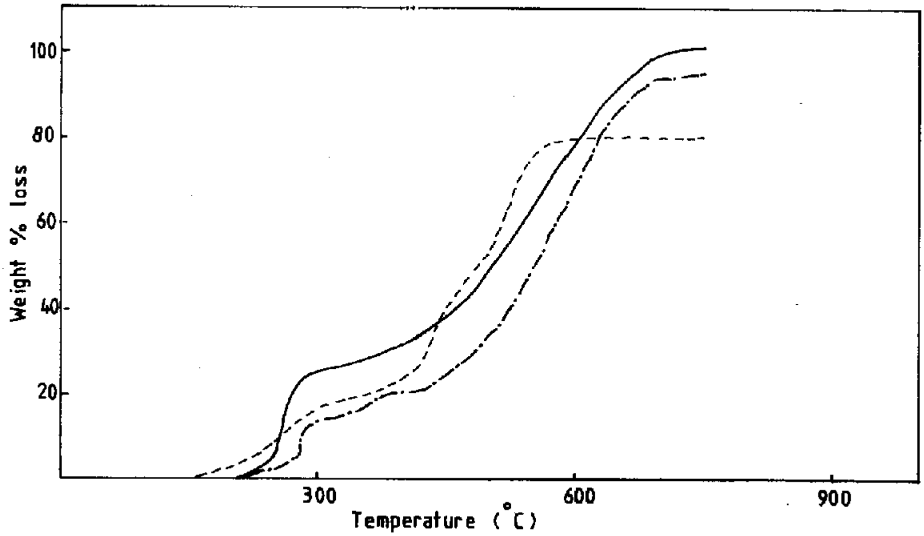


Fig. 1. Typical thermogravimetric curves for the 5% copolymer before grafting (- - - - - -), polyacrylonitrile (·—·—·), and thermografted copolymer sample No. 8 ($\bar{X}_g$ = 370) (———).

TABLE 2

The effect of grafting temperature on the average degree of grafting, $\bar{X}_g$

Temp. (°C)	53	69	81	101
$\bar{X}_g$	0.42	1.84	2.12	1.11
$[\eta]$ ($cm^3\ g^{-1}$)	58.5	59.2	59.2	59.0

Reaction time = 17 h, $[I] = 10^{-4}$ mol, $[M] = 0.09$ mol.

TABLE 3

The effect of grafting time on $\bar{X}_g$

Grafting time (h)	18	23	43	66
$\bar{X}_g$	12	104	213	370
$[\eta]$ ($cm^3\ g^{-1}$)	63.5	107.2	140.3	155.0

$[M] = 1$ mol at 81°C, $[I] = 10^{-4}$ mol.

TABLE 4

The effect of acrylonitrile concentration on $\bar{X}_g$

Acrylonitrile (mol) [M]	0.56	0.18	0.09	0.04
$\bar{X}_g$	257	2.7	2.1	0.2
$[\eta]$ ($cm^3\ g^{-1}$)	144.2	60.3	59.2	58.8

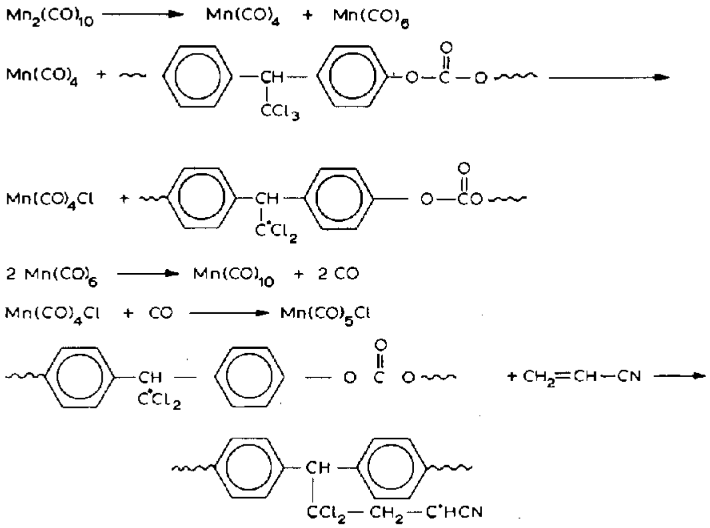
At 81°C for 17 h, $[I] = 10^{-4}$ mol.

On the other hand, the reaction time has a remarkable effect on $\bar{X}_g$ (Table 3).

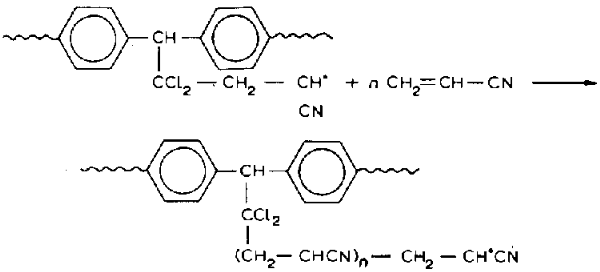
The other factor notably affecting $\bar{X}_g$ was the acrylonitrile monomer concentration (Table 4).

The mechanism of thermografting could display the following scheme.

Initiation step



Propagation



Termination

The termination reactions could be characterised either by coupling, disproportionation and/or by chain transfer to monomer, solvent or to the polymer chains.

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