Carbenoid Polycondensation

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A series of poly(alkylene fumarate/maleate)s are produced by a polycondensation reaction of alkoxycarbonyl carbenoid intermediates generated through α,α-dichloro elimination from dichloroacetic acid diesters by treatment with copper metal in dimethyl sulphoxide.

Carbenoids are recognized as key reactive intermediates in a variety of transition metal catalysed polymerization reactions, such as the ring opening metathesis polymerization of cyclic alkenes[1,2] and presumably also Ziegler–Natta type polymerizations of alkenes and alkynes.[3] However, examples of efficient polymerization systems involving a carbenoid coupling reaction as an elementary polymerization process are rare. The poor reaction selectivity of conventional carbenoid coupling processes is the cause of this. Even minimal side reactions in an elementary step reduce the degree of polymerization of the product.

The present Communication describes a new polymerization reaction system, in which an exceptionally selective carbenoid coupling reaction[4] constitutes an elementary

Table 1. Carbenoid polycondensation of dichloroacetic acid diesters, **1**[a]

Run	Monomer	Time (h)	D.p.[b,c]	Yield[d] (%)	*E*-form ratio[b] (%)
1	**1a**	3	3.9	77	84
2	**1a**	18	24.3	74	87
3	**1b**	18	12.2	33	73
4	**1c**	18	7.3	72	80

[a] Dichloroacetic acid diesters: 20 mmol, copper powder (200 mesh): 60 mmol, DMSO: 20 ml, 25 °C. [b] ^{1}H NMR (270 MHz, CD_3OCD_3, 40 °C). [c] D.p. represents degree of polymerisation. [d] (Isolated product in g)/(Calculated amount by the formula with obtained d.p., in g).

step in the polymerization process, and which may be termed 'carbenoid polycondensation'.[5] [See eqn. (1).]

$$\begin{array}{ll} \mathrm{Cl_2CHCO_2(CH_2)_nOCOCHCl_2} \xrightarrow[\text{DMSO}]{\text{Cu}} & \\ \quad \mathbf{1};\ \mathbf{a}: n = 2 & \\ \quad \mathbf{b}: n = 4 & -[\mathrm{CHCO_2(CH_2)_nOCOCH}]-_m \qquad (1) \\ \quad \mathbf{c}: n = 8 & \quad \text{poly-}\mathbf{1} \end{array}$$

Thus, a series of dichloroacetic acid diesters were synthesized† and treated with copper metal in dimethyl sulphoxide (DMSO). The copper dissolved to form a dark green $CuCl_2(DMSO)_2$ complex.[6] The reaction mixture was then poured into water to isolate the product, which was further purified by dry column chromatography technique on silica gel.‡ The resinous or powdery products obtained were characterized by ^{1}H and ^{13}C NMR, IR and GPC (gel permeation chromatography) analyses. For example, ^{1}H NMR of the product obtained from ethylene glycol bis(dichloroacetate), **1a**, showed alkenic signals corresponding to *Z*(maleic) and *E*(fumaric) forms at δ 6.45 and 6.84, respectively.[7] The degree of polymerization of poly-**1a** could be determined by comparison of the signal intensity ratio between dichloromethyl protons at δ 6.56 due to end groups and the above-mentioned alkenic protons. The structure of the product was confirmed also by the presence of ^{13}C NMR signals due to maleic(130.8) and fumaric(134.2) carbon atoms were present along with dichloromethyl carbons (65.6). An IR analysis of poly-**1a** showed an absorption at 1720 cm^{-1} due to the conjugated carbonyl groups, and at 3090 and 1640 cm^{-1} due to alkenic groups. GPC analysis of poly-**1a** showed a regular distribution pattern and the increase in the average molecular weight with reaction time, indicative of the selective carbenoid coupling reaction in the present system.

The results for carbenoid coupling reactions with a series of dichloroacetic acid diesters are summarized in Table 1. The coupling reaction was found to take place at an ambient temperature to produce corresponding unsaturated polyesters in appreciable yields and with a degree of substitution up to 24. The *E*-form along the product chain was found to be predominant as was the case for the reaction with dichloroacetic acid monoesters reported previously.[4]

In conclusion, the present carbenoid polycondensation process can offer a new methodology for macromolecular synthesis and can extend the choice of a monomer reagent in polymerization reactions.

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† Dichloroactic acid diesters, **1a–c**, were synthesized by the reaction of the corresponding diols and dichloroacetyl chloride in acetone in the presence of pyridine and were purified by dry chromatography on silica gel with dichloromethane as an eluent. **1a**; ^{1}H NMR (270 MHz, $CDCl_3$, 40 °C) δ 6.00(1H, s), 4.54(2H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$, 40 °C) δ 164.1, 64.0, 63.7. **1b**; ^{1}H NMR δ 5.97(1H, s), 4.31(2H, t), 1.83(2H, m). ^{13}C NMR δ 164.2, 66.5, 64.1, 24.6. **1c**; ^{1}H NMR δ 5.97(1H, s), 4.28(2H, t), 1.73(2H, m), 1.37(4H, broad). ^{13}C NMR δ 164.4, 67.5, 64.3, 28.8, 28.1, 25.4.

‡ The purification of the products was performed first by precipitation into water, filtration with a fine-mesh glass filter, followed by ultracentrifuge at 3000 rpm for 20 min. The product was subjected to dry chromatography on silica gel (70–230 mesh, Nacalai Tesque) with acetone or methylethyl ketone as eluent.