Synthesis of Unsaturated Polyesters through the Polycondensation of Carbenoid Intermediates†

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ABSTRACT: A series of dichloroacetic acid diesters ($Cl_2CHCO_2ROCOCHCl_2$, R = $(CH_2)_n$, n = 2, 3, 4, 8, and 1,4-cyclohexyl), **1a–e**, were treated with copper metal in DMSO to produce the corresponding poly(alkylene fumarate/maleate), **2**, through a polycondensation reaction of carbalkoxy carbenoid intermediates generated via α,α-dichloro elimination from **1**. The random and block type unsaturated copolyesters were also produced through the simultaneous and the consecutive additions of different types of **1**, respectively.

Introduction

Carbenoids are recognized as key reactive intermediates in a variety of transition metal catalyzed polymerization reactions, including the ring-opening metathesis polymerization of cyclic alkenes[1] and presumably a Ziegler–Natta type polymerization of alkenes and alkynes.[2] The metathesis reaction with acyclic diene derivatives has also been applied for the synthesis of unsaturated polyester and polyether derivatives.[3] There have been, however, few examples of efficient polymerization systems involving a carbenoid coupling reaction as an elementary polymerization process.[4] This is obviously due to too poor reaction selectivity of the conventional carbenoid coupling process to apply for the polymer synthesis since even minimal side reactions in an elementary step strongly suppress the degree of polymerization of the product.

We have recently reported a novel reaction system in which a carbenoid coupling reaction takes place in an almost quantitative yield when dichloroacetic acid esters are treated with copper metal in DMSO.[5] By making use of this new reaction system, we have developed a novel polymerization system by using dichloroacetic acid diesters as "monomers" in which a successive carbenoid coupling reaction takes place with a high selectivity, leading to the formation of macromolecular products. This polymerization system may be termed "carbenoid polycondensation".[6]

In the present paper, we report the detailed study on this carbenoid polycondensation system by employing various types of dichloroacetic acid diesters as "monomers". We also present the results on the copolycondensation reaction by using two different types of "monomers", where both random and block type unsaturated polyester derivatives are produced either by the simultaneous or by the consecutive addition of "monomers".

Experimental Section

Materials. Ethylene glycol, 1,3-propanediol, and 1,4-butanediol were distilled before use, and 1,8-octanediol, 1,4-cyclohexanediol, hydroquinone, and Bisphenol A were used as received. DMSO was distilled under reduced pressure and stored under a dry N_2 atmosphere. Copper metal used in the present study was in the powder form (250 mesh, Merck) and was used without further purification. Other reagents were purified by conventional procedures.

A series of dichloroacetic acid diesters (**1a–g**) were prepared by the reaction of the corresponding diols with dichloroacetyl chloride in the presence of pyridine. Thus, in a 1-L three-neck flask equipped with a dropping funnel, a reflux condenser, and a mechanical stirrer, 10.53 g (0.17 mol) of ethylene glycol and 26.81 g (0.34 mol) of dry pyridine were mixed in 400 mL of dry acetone and cooled in an ice/water bath. Thereupon 50.00 g (0.34 mol) of dichloroacetyl chloride was added dropwise under stirring to form a white precipitate. The reaction mixture was then heated to reflux for 2 h. The reaction product was extracted with ether after adding 150 mL of water to dissolve the precipitated product into the reaction medium. The combined ethereal solution was treated with 10% aqueous H_2SO_4 and dried over Na_2SO_4 for one night. After ether was removed by evaporation, the reaction product was finally purified by means of a dry column chromatography technique[5] (column, i.d. 40 mm; length, 100 cm) on silica gel (70–230 mesh, Nacalai Tesque). **1a**: yield 92.4%; ^{1}H-NMR ($CDCl_3$, 40 °C) δ = 6.00 (1 H, s), 4.54 (2 H, s); ^{13}C-NMR ($CDCl_3$, 40 °C) δ = 164.1, 64.0, 63.7; IR 1765 (C=O), 1165 (C–O) cm^{-1}.

Other dichloroacetic acid diesters (**1b–g**) were prepared by a similar procedure. **1b**: yield 86.4%; ^{1}H-NMR ($CDCl_3$, 40 °C) δ = 5.99 (1 H, s), 4.40 (2 H, t), 2.17 (1 H, m); ^{13}C-NMR ($CDCl_3$, 40 °C) δ = 164.2, 64.0, 63.5, 27.3; IR 1765 (C=O), 1165 (C–O) cm^{-1}. **1c** (the reaction was carried in ether solution): yield 91.2%; ^{1}H-NMR ($CDCl_3$, 40 °C) δ = 5.97 (1 H, s), 4.31 (2 H, t), 1.83 (2 H, m); ^{13}C-NMR ($CDCl_3$, 40 °C) δ = 164.2, 66.5, 64.1, 24.6; IR 1760 (C=O), 1170 (C–O) cm^{-1}. **1d**: yield 60.0%; ^{1}H-NMR ($CDCl_3$, 40 °C) δ = 5.97 (1 H, s), 4.28 (2 H, t), 1.73 (2 H, m), 1.36 (4 H, broad); ^{13}C-NMR ($CDCl_3$, 40 °C) δ = 164.4, 67.5, 64.3, 28.8, 28.1, 25.4; IR 1760 (C=O), 1170 (C–O) cm^{-1}. **1e**: yield 65.3%; ^{1}H-NMR ($CDCl_3$, 40 °C) δ = 5.99 (1 H, s), 5.04 (1 H, broad), 1.78–2.09 (4 H, m); ^{13}C-NMR ($CDCl_3$, 40 °C) δ = 163.7, 73.6 + 73.4, 64.5, 26.7 + 26.0; IR 1740 (C=O), 1180 (C–O) cm^{-1}. **1f** (the reaction product was obtained partly as a precipitate in the reaction mixture after adding water, and the remainder was recovered by extraction with ether; then the product was purified by reprecipitation from acetone/methanol): yield 59.7%; ^{1}H-NMR (DMSO-d_6, 40 °C) δ = 7.37 (2 H, s), 7.14 (1 H, s); ^{13}C-NMR (DMSO-d_6, 40 °C) δ = 167.2, 151.8, 126.4, 68.8; IR 1770 (C=O), 1170 (C–O) cm^{-1}. **1g**: yield 70.6%; ^{1}H-NMR ($CDCl_3$, 40 °C) δ = 7.06–7.27 (4 H, q (AB)), 6.12 (1 H, s), 1.68 (3 H, s); ^{13}C-NMR ($CDCl_3$, 40 °C) δ = 162.9, 148.8, 148.2, 128.0, 120.2, 64.2, 42.6, 30.8; IR 1755 (C=O), 1170 (C–O) cm^{-1}.

Procedures. Homopolycondensation. In a 100-mL round-bottom flask, a weighed amount (20 mmol) of **1** and 20 mL of DMSO were mixed, and a prescribed amount of copper powder was added to start the reaction with stirring under a N_2 atmosphere in a thermostated bath. The gradual dissolution of copper metal was observed to result in a dark-green, almost homogeneous solution. The crude reaction product was recovered by pouring the reaction solution into water and was rinsed with ca. 20 mL of methanol. The recovered product was then

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† Part 2 of "Carbenoid Polycondensation". For Part 1, see ref 6. The paper is dedicated to the memory of Professor G. Smets.

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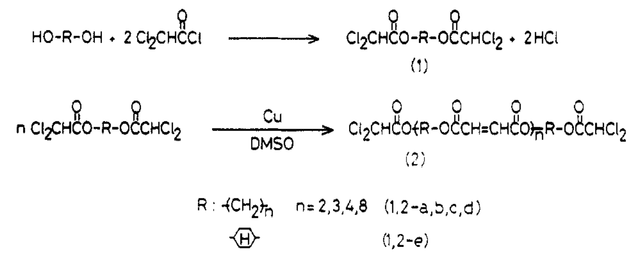
Scheme I



suspended in methyl ethyl ketone and subjected to centrifuge treatment at 3000 rpm for 20 min. Thereafter the supernatant solution was concentrated, and dry column chromatography on silica gel was carried out, followed by freeze-drying from benzene solution to yield a purified product.

Copolycondensation. Two different copolymerization procedures, i.e., the simultaneous reaction and the consecutive reaction, were employed with two different types of 1.

Simultaneous Reaction. In a 100-mL round-bottom flask, weighed amounts of two types of 1 (10 mmol each) and 20 mL of DMSO were mixed, and 3.81 g (60 mmol) of copper powder was added to start the reaction. The reaction was stirred for 18 h at 25 °C. The reaction product was isolated and purified by the procedure described in the homopolycondensation.

Consecutive Reaction. In a 100-mL round-bottom flask, a weighed amount (10 mmol) of one type of 1 and 10 mL of DMSO were mixed, and 1.91 g (30 mmol) of copper powder was added to start the reaction. The reaction was stirred for 10 h at 25 °C. Subsequently, another type of 1 (10 mmol), 10 mL of DMSO, and 1.91 g of copper powder were added to the reaction mixture and the reaction was allowed to continue for another 10 h. The reaction product was isolated and purified as in the simultaneous reaction.

Measurements. ^{1}H- and ^{13}C-NMR measurements were performed with a JEOL GX-270 apparatus at 270 MHz for ^{1}H and 67.5 MHz for ^{13}C. Chemical shifts (in ppm) were calibrated from the signals of either $CDCl_3$ (7.30 for ^{1}H and 77.0 for ^{13}C) or DMSO-d_6 (2.50 for ^{1}H and 43.5 for ^{13}C). IR spectra were taken on a Shimadzu FT-IR Model 8100. GPC measurements were carried out with a Tohso high-performance liquid chromatograph Model 803C equipped with RI (Tohso Model RI-8) and UV (Tohso Model UV-8, at 254 nm) detectors and with a column of either TSK G2000HXL or TSK G3000HXL. The eluent was THF at a flow rate of 1.0 mL/min.

Results and Discussion

Homopolycondensation. A series of dichloroacetic acid diesters (**1a–g**) were prepared by reaction of the precursor diols, i.e., a series of alkylene glycols as well as hydroquinone and Bisphenol A, with dichloroacetyl chloride in the presence of pyridine (Scheme I). They could be conveniently purified by a dry column chromatography technique on silica gel. The obtained **1** was then subjected to reaction with copper metal in DMSO in the moderate temperature range from 25 to 50 °C. A gradual dissolution of copper into the reaction medium was observed to indicate the formation of $CuCl_2(DMSO)_2$ complex.[7] The reaction product, **2**, was then isolated by pouring the reaction mixture into water, followed by purification by dry column chromatography on silica gel. The resinous or powdery products thus obtained were analyzed by ^{1}H- and ^{13}C-NMR, IR, and GPC techniques.

Figure 1 shows the ^{1}H-NMR spectrum of **2b**, in which olefinic proton signals due to the *Z* (maleic) and *E* (fumaric) forms are present at 6.25 and 6.84 ppm, respectively.[8] This clearly indicates the formation of poly(alkylene fumarate/maleate) through the coupling reaction of the carbenoid intermediates generated by α,α-dichloro elimination from **1b**. The degree of polymerization (*n* in Scheme I) of the products could be estimated by comparing the signal intensity ratio between the dichloromethyl proton at 5.98 ppm from the end group of the product and the above-mentioned olefinic protons. The yield of the products (Table I; vide infra) was estimated by deducting the amount of the eliminated chlorine atoms in the product of a given degree of substitution determined by the above NMR measurements.

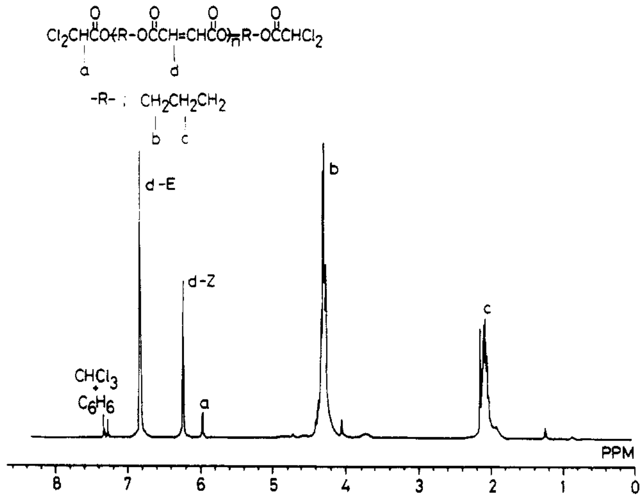


Figure 1. 270-MHz ^{1}H-NMR spectrum of the carbenoid polycondensation product from **1b** (sample, run 13 in Table I; $CDCl_3$, 40 °C).

Table I
Homopolycondensation of Dichloroacetic Acid Diesters 1[a]

run	1	Cu/1 (mol/mol)	temp (°C)	time (h)	yield[b] (%)	M_n (DP)[c]	*E*-form ratio[d]
1	**1a**	1.0	25	3	64	360 (0.5)	90
2	**1a**	2.0	25	3	69	500 (1.6)	82
3	**1a**	3.0	25	3	77	840 (3.9)	84
4[e]	**1a**	3.0	25	3	69	2980 (19.0)	75
5	**1a**	4.0	25	3	89	1730 (10.4)	80
6	**1a**	3.0	25	6	90	1400 (7.9)	83
7	**1a**	3.0	25	12	81	2030 (12.3)	84
8	**1a**	3.0	25	18	74	3730 (24.3)	87
9	**1a**	3.0	25	100	31	6250 (42.0)	70
10	**1a**	3.0	35	3	96	1320 (7.3)	84
11	**1a**	3.0	45	3	65	3360 (21.7)	89
12	**1a**	3.0	50	3	49	6400 (43.0)	89
13	**1b**	3.0	25	18	35	1910 (10.3)	68
14	**1b**	3.0	50	3	30	2250 (12.5)	86
15	**1c**	3.0	25	3	87	470 (1.0)	79
16	**1c**	3.0	25	18	33	2400 (12.2)	73
17	**1c**	3.0	35	3	60	1120 (4.8)	81
18	**1c**	3.0	50	3	31	1770 (8.6)	78
19	**1d**	3.0	25	18	72	2010 (7.3)	80
20	**1d**	3.0	50	3	86	1310 (4.2)	83
21	**1e**	3.0	25	18	44	2000 (8.4)	77
22	**1e**	3.0	50	3	32	1920 (8.1)	78

[a] 1, 20 mmol; DMSO, 20 mL. [b] Based on the product structure of a given DP estimated by ^{1}H-NMR. [c] *n* in Scheme I, by ^{1}H-NMR. [d] By ^{1}H-NMR. [e] With sonication.

Figure 2 shows the ^{13}C-NMR spectrum of **2a** having the degree of polymerization of 24.3, where the structure of the product was again confirmed by the presence of signals due to *Z* (maleic) and *E* (fumaric) carbons at 129.6 and 133.3 ppm, respectively, and of the weak signal due to the dichloroacetyl carbon at 64.0 ppm located at the end of the product.

The IR spectrum of **2a** is shown in Figure 3 together with that of the starting **1a**, where the absorption at 3080 and 1645 cm^{-1} due to the olefinic groups appears in **2a** and that of the carbonyl groups shifts from 1765 cm^{-1} for **1a** to 1720 cm^{-1} for **2a** along with the formation of the conjugated fumaric/maleic ester groups. The presence of the absorption at around 3500 cm^{-1} for **2a**, assignable to hydroxyl groups, suggests the concurrent hydrolysis of

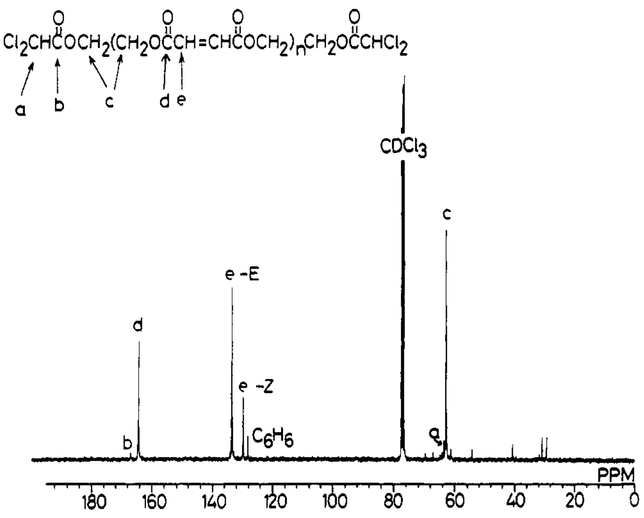


Figure 2. 67.5-MHz ^{13}C-NMR spectrum of the carbenoid polycondensation product from **1a** (sample, run 8 in Table I; CDCl$_3$, 40 °C).

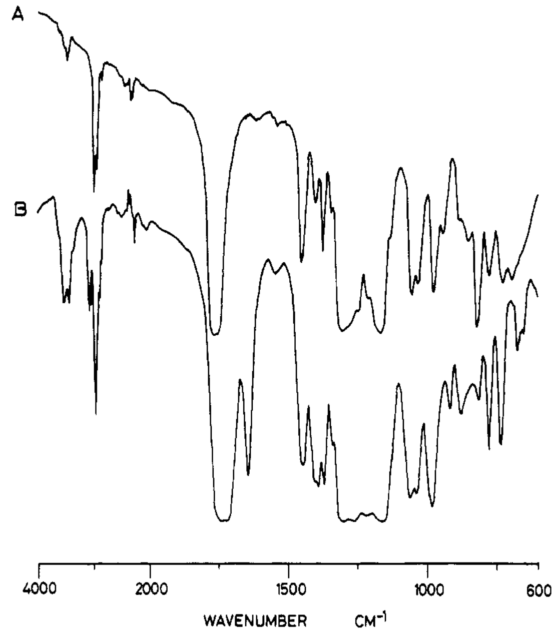


Figure 3. IR spectra of (A) **1a** and (B) the carbenoid polycondensation product (sample, run 8 in Table I).

the product or the chain termination in the course of the reaction.

An example of the GPC inspection of **2a** is shown in Figure 4 to demonstrate the regular distribution pattern of the product from monomer to n-mer in the RI trace, while peaks from dimer to n-mer were observed in the UV trace, according with the presence of UV-sensitive olefinic groups solely in the coupling product. Also the GPC pattern shifted to the higher molecular weight region with increasing reaction time. These GPC results appear to exclude the presence of cyclic oligomers with a certain preferential ring size frequently observed in conventional polycondensation reactions.

The results on the present carbenoid polycondensation reaction using a series of **1** and under various reaction conditions with, in particular, **1a** are summarized in Table I. The selective coupling reaction was found to proceed with dichloroacetic acid diesters from aliphatic diols, **1a–e**, at ambient or slightly elevated temperature to produce the corresponding unsaturated polyesters in appreciable isolated yields. On the other hand, dichloroacetic acid diesters from hydroquinone and from Bisphenol A, **1f** and **1g**, failed to give a noticeable amount of polymeric products. This is relevant to the lower selectivity in the coupling reaction with a phenyl derivative of dichloroacetate compared to alkyl derivatives.[5]

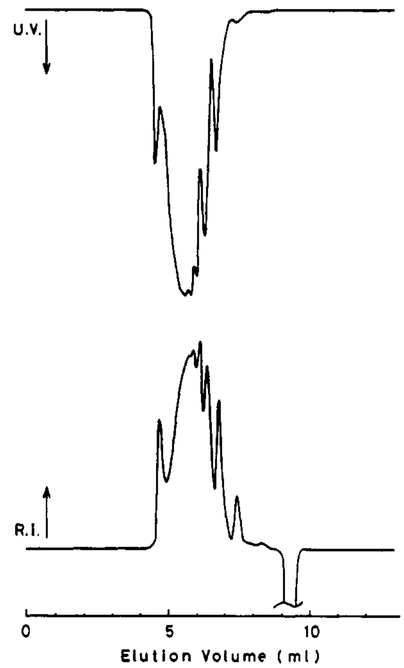


Figure 4. GPC trace of the carbenoid polycondensation product from **1a** with RI and UV detectors (sample, run 3 in Table I; column, TSK G2000HXL; eluent, THF, 1.0 mL/min; exclusion limit volume, 4.5 mL).

Reaction conditions such as the charged ratio between copper and **1a** (runs 1–5), the reaction time (runs 6–9), and the reaction temperature (runs 10–12) were varied, and a remarkable increase in the degree of polymerization of the product (n in Scheme I) was observed with the use of an excess amount of copper vs **1a**, with prolonged reaction time, or at elevated temperature. Thus, products possessing a degree of polymerization as high as around 40 were produced. Sonication of the reaction medium was also found to accelerate the reaction. In addition, it was noticed that the molecular weight of the isolated reaction product appeared to decrease with increasing alkyl chain length in **1**.

The E-form stereochemistry of olefinic groups along the product chain was found to be predominant in all cases, as was the case in the reaction with dichloroacetic acid monoester derivatives reported before.[5]

In the present system, the lifetime of the carbenoid intermediate species generated in the medium is considerably long, since it survives during the chain-growing process through a bimolecular reaction mechanism. The stable nature of the present carbenoid species agrees with the observation that no cycloaddition occurred in the presence of cyclohexene.[5] A further study to elucidate the nature of the carbenoid species generated in the present system is now underway.

Copolycondensation. The copolymerization reaction using two different types of **1** was carried out by the following two procedures: one involved the simultaneous addition of a mixture of different types of **1** to start the reaction, and the other involved the consecutive addition of different types of **1** in the course of the reaction (Scheme II). The former process is expected to give a random copolyester, and the latter a block copolyester.

The structural feature of random and block type copolyester products was confirmed by ^{1}H- and ^{13}C-NMR, and the results are shown in Figures 5 and 6. In Figure

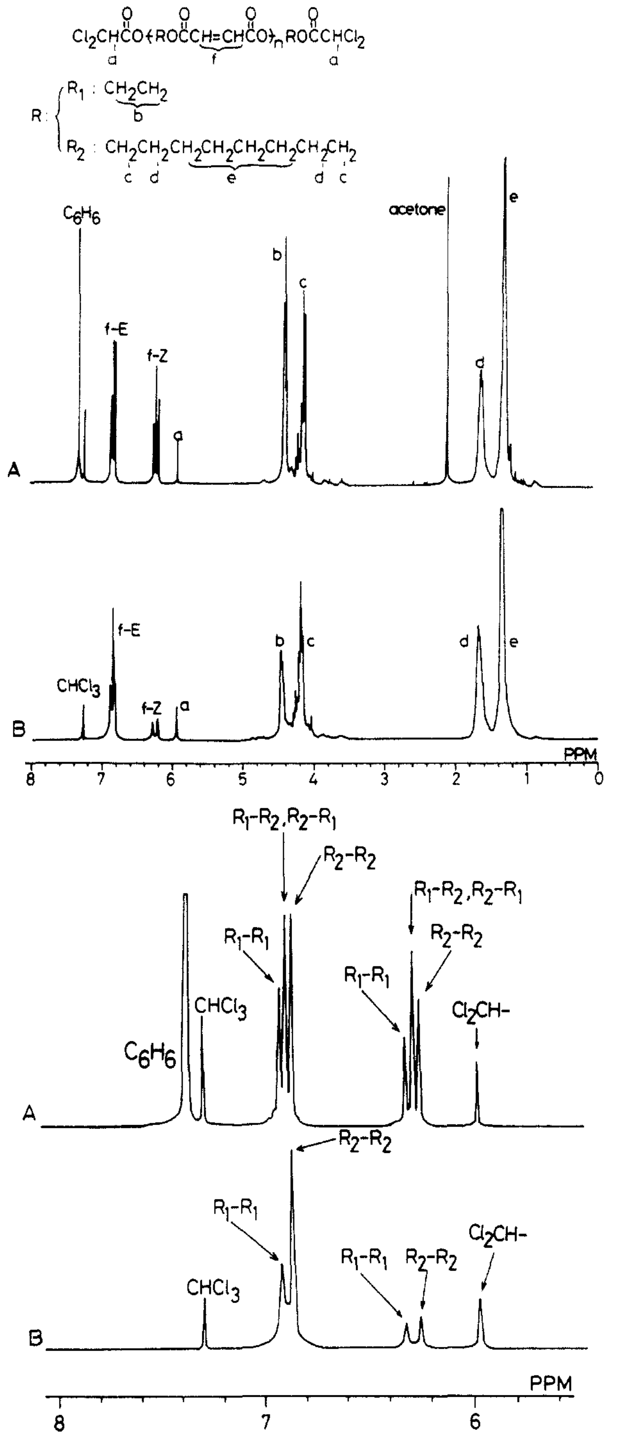
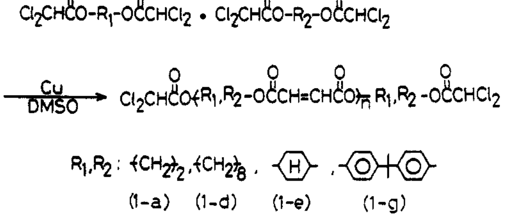


Figure 5. 270-MHz ^{1}H-NMR spectra of the copolycondensation product from **1a** and **1d** (A) by the simultaneous procedure and (B) by the consecutive procedure, (samples, runs 1 and 4 in Table II; CDCl$_3$, 40 °C). (a, Top) Full range; (b, bottom) olefinic proton area.

Scheme II



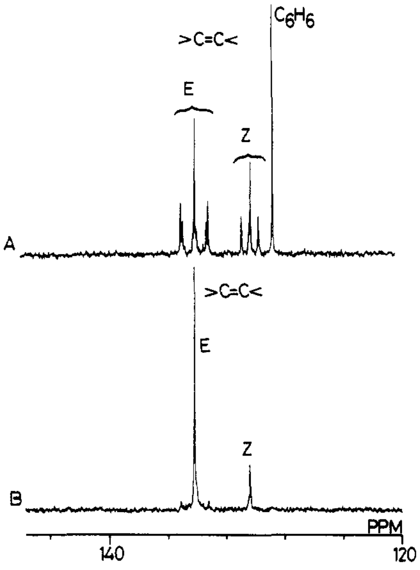


Figure 6. 67.5-MHz ^{13}C-NMR olefinic carbon area spectra of the polycondensation product (A) by the simultaneous procedure and (B) by the consecutive procedure (samples, runs 1 and 4 in Table II; CDCl$_3$, 40 °C).

5a, the full-range ^{1}H-NMR spectra of the products obtained by the simultaneous and by the consecutive addition of **1a** and **1d** are compared. The degree of polymerization and the stereochemistry of the product were readily estimated, as in the homopolycondensation product. Furthermore, close examination of the olefinic region in the spectra shown in Figure 5b demonstrates the random and block nature of the comonomer unit distribution in the product chain.[9] Thus, a triplet pattern was observed for the former in both the *E* and *Z* forms of the olefinic signals, corresponding to the presence of **1a**/**1a**, **1a**/**1d**, and **1d**/**1d** sequences, while a doublet was observed for the latter, corresponding to the presence of solely **1a**/**1a** and **1d**/**1d** sequences.

In Figure 6, ^{13}C-NMR olefinic region spectra of the products obtained by the simultaneous and by the consecutive addition procedures are compared. Thus, a triplet pattern was observed for the former in both the *Z* and *E* forms of the olefinic signals, which is accounted for by the overlapping of the singlet due to the symmetric (**1a**/**1a** and **1d**/**1d**) structure and the doublet due to the dissymmetric (**1a**/**1d**) structure, while the singlet for the latter is due to the presence of solely the symmetric structure.

The results for copolycondensation reactions using different types of **1** are summarized in Table II. The random copolycondensation of the two types of aliphatic diol derivatives, i.e., **1a** with either **1d** or **1e**, was found to produce the corresponding unsaturated copolyesters, and the reactivity of different types of **1** was observed to be almost identical (runs 1 and 2). The *E*-form content in the olefinic groups in the product chain was slightly lower than in the homopolycondensation products, **2a**, **2d**, and **2e**. The Bisphenol A derivative, **1g**, copolymerized with **1a** to produce the unsaturated copolyester product (run 3), though **1g** by itself failed to produce the homopolymer product.

The consecutive addition of different types of **1** produced a series of block type unsaturated copolyesters (runs 4–6). In the consecutive reactions of **1a** with either **1d** or **1e**, the former was observed to be less reactive than either of the latter, while the stereochemistry of the product chain was almost identical to those in the relevant homopolycondensation products, in contrast to the random copolyester products. The cause of the apparent disagreement in the reactivity of **1** in the random and block copolymerization process is yet obscure but will be relative to the specific

Table II
Copolycondensation of Dichloroacetic Acid Diesters 1[a]

	1^c						
run[b]	R_1	R_2	time (h)	yield[d] (%)	M_n (DP)[e]	R_1/R_2 ratio in the product (mol/mol)	*E*-form ratio[f]
1	**1a** + **1d**		18	74	3460 (17.1)	0.91	64
2	**1a** + **1e**		18	86	4200 (23.2)	0.93	66
3	**1a** + **1g**		18	25	5900 (19.0)[g]	0.69	*h*
4	**1a** , **1d**		10 + 10	61	2100 (9.4)	0.46	80
5	**1d** , **1a**		10 + 10	47	2650 (10.9)	1.80	82
6	**1a** , **1e**		10 + 10	60	1700 (7.0)	0.67	81

[a] **1**, 10 mmol each; DMSO, 20 mL in total; Cu/**1** ratio, 3.0 (mol/mol); temperature, 25 °C; for further details, see Experimental Section. [b] Runs 1–3, simultaneous reaction; runs 4–6, consecutive reaction. [c] For R_1 and R_2, see also Scheme II. [d] Based on the product structure of a given DP estimated by ^{1}H-NMR. [e] *n* in Scheme II, by ^{1}H-NMR. [f] By ^{1}H-NMR. [g] By GPC, with polystyrene standard calibration. [h] Not determined.

influence of the initially formed product on the subsequent coupling reaction, as was noted before in the reaction with dichlorodiphenylmethane.[5]

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

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