Cationic Copolymerization of Methyl Glyoxylate with 1,3-Dioxolane

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ABSTRACT: Cationic copolymerization of methyl glyoxylate (GM), an aldehyde containing an ester group in addition to aldehyde function, with cyclic acetal, 1,3-dioxolane (DXL), was studied. Resulting copolymers after hydrolysis of the ester groups provide hydrophilic, degradable polymers containing ionic functions. It has been shown that despite the reversibility of homopropagation steps for both comonomers the conversion of both comonomers in copolymerization can be nearly quantitative. Molecular weights of copolymers are relatively high (up to 1.7×10^4), although lower than that calculated for polymerization proceeding without transfer. It was established that chain transfer involves hydride ion abstraction from the GM monomer or from the GM repeating unit of the copolymer. Polymerization is accompanied by extensive chain transfer to polymer (transacetalization). Intramolecular reaction (backbiting) leads to formation of a cyclic fraction, of which the major component (the only one observed) is a heterodimer, in other words, a seven-membered cyclic acetal composed of one GM and one DXL unit. Intramolecular chain transfer to the polymer leads to redistribution of comonomer units, and copolymers having nearly random distribution are formed (with a slight tendency for alternation due to the steric repulsion between bulky substituents in the GM−GM homodiads).

Introduction

Only a few aldehydes are known to give high-molar-mass polymers.[1−3] This is due to the high reversibility of aldehyde polymerization. Therefore, even if polymer is obtained at, for example, low temperature, it is then inherently unstable under normal conditions, undergoing spontaneous depropagation (sometimes called unzipping). This process can be stopped by end-capping; however, chain scission (e.g., following oxidation) generates new weak points at which unzipping could start.

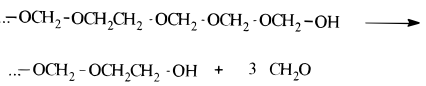
Thermally unstable polyacetals, for example, polyformaldehyde, can be stabilized through copolymerization with another monomer leading to macromolecules in which the unzipping process stops, when a comonomer unit is reached during the depropagation, providing that unzipping involving comonomer unit is thermodynamically less favorable;[4,5] see Scheme 1.

Recently, polymerization of an aldehyde containing an ester group, namely, methyl glyoxylate (GM), was studied.[6,7] The corresponding polymer, prepared by either anionic or cationic polymerization, could be stabilized by blocking the end groups. The polymer itself is an interesting example of a functional polyacetal, in which the ester group can be used for further modification.

Copolymerization of aldehydes with cyclic compounds has not been studied, with the only exception being copolymerization of formaldehyde or its trimer (1,3,5-trioxane) with cyclic acetals or cyclic ethers.[5]

It became thus of interest to establish whether it is possible to prepare a GM copolymer with a monomer that would stop, as indicated above, the unzipping process. We have chosen for this copolymerization the cationic process and 1,3-dioxolane (DXL) as the comonomer. After hydrolysis of the ester group, this should lead to thermally stable hydrophilic copolymers containing ionic functions.

Scheme 1



Experimental Section

Methyl glyoxylate (kindly provided by former Societe Francaise Hoechst, now Clariant) is a mixture of oligomers in form of a viscous liquid (GM undergoes spontaneous polymerization upon storage). Monomeric GM was obtained by depolymerization, proceeding in the course of vacuum distillation over P_2O_5. The fraction boiling at ≅44 °C under 45 mbar was collected and used for the copolymerization experiments. GM was stored in a closed ampule under vacuum at −5 °C.

1,3-Dioxolane (Aldrich) was purified by refluxing over CaH_2 followed by distillation (bp = 74−75 °C) to the ampule over a sodium mirror. It was subsequently condensed on the vacuum line and stored in a closed ampule under vacuum over a sodium−potassium alloy.

Trifluoromethanesulfonic acid (triflic acid, TfA) (Aldrich) was purified by distillation (bp = 162 °C) and distributed into phials sealed under vacuum.

Dichloromethane (CH_2Cl_2) was washed with concentrated sulfuric acid to remove unsaturated impurities. This procedure was repeated until the acid layer remained colorless. CH_2Cl_2 was subsequently washed with water, 5% wt aqueous $NaHCO_3$, and again with distilled water. After preliminary drying with $CaCl_2$ for 24 h, methylene dichloride was refluxed over CaH_2 for 6 h and distilled. The fraction boiling at 39.5−40 °C was collected in an ampule containing fresh CaH_2. Finally, CH_2Cl_2 was condensed on a vacuum line into an ampule over a sodium mirror.

Copolymerizations were carried out in ampules sealed under vacuum. The typical experimental procedure was as follows: the phial containing initiator was placed together with a glass-covered iron bar (allowing breaking of the phial with a magnet) inside an ampule equipped with a Rotaflo stopcock. After being connected to a vacuum line, required amounts of GM, DXL,

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and CH_2Cl_2 were distilled into the ampule. The ampule was placed in a cooling bath, and the phial containing the initiator was broken to start the reaction. Copolymerization was terminated by addition of 5-fold excess (with respect to acid) of CH_3ONa dissolved in CH_3OH (approximately 5% wt solution). Copolymers were isolated by evaporation of solvents (in some cases also the unreacted monomers) using rotary evaporator.

In an attempted synthesis of block copolymers, a similar procedure was used. Thus, first the solution of DXL in CH_2Cl_2 was allowed to polymerize with TfA as the initiator. After the required period of time, the ampule was filled with dry argon, and a sample of the solution was withdrawn. In this sample, polymerization was terminated as described above, and a homopolymer of DXL was isolated and analyzed. The ampule containing the remaining part of the solution was evacuated on the vacuum line at −78 °C, and then, GM was distilled into this ampule from a calibrated cylinder attached to the vacuum line. After the solution was brought to the desired temperature, the second stage of sequential copolymerization was conducted. Copolymerization was terminated in the same way as described above.

Mass spectra were recorded with Finnigan MAT95 apparatus using chemical ionization with isobutane. In the mass spectrum of heterodimer, the signal of parent ion at $m/e = 163$ (M + 1) was observed, together with signals corresponding to the fragmentation products at m/e = 133 (elimination of $-OCH_2$), 89 (elimination of a DXL unit), and 75 (elimination of a GM unit).

Elemental analysis of a heterodimer gave the following values: %C = 44.15%, %H = 6.02%, %O = 49.83% (calcd: %C = 44.44%, %H = 6.18%, %O = 49.38%).

NMR spectra were recorded with Bruker 200 AC 200 (200 MHz for ^{1}H and 50.33 MHz for ^{13}C) and Bruker DRX 500 (500 MHz for ^{1}H and 125.77 MHz for ^{13}C) with proton decoupling for ^{13}C NMR spectra.

UV spectra were recorded with Hewlett-Packard 8452 A spectrometer. The heterodimer, due to the presence of the −CH═O group, shows UV absorption at $\lambda_{max} = 234$ nm. The extinction coefficient is $\epsilon = 52$ L mol^{-1} cm^{-1}.

Gas liquid chromatography (GLC) analysis was performed with Varian Aerograph 2700 instrument (FID detection) connected to LDC 308 integrator using 10 m columns filled with 10% OV 101.

Results and Discussion

It has been previously shown that TFA is an efficient initiator of cationic homopolymerization of GM.[6,7] Homopolymerization of GM initiated with TFA proceeds relatively quickly: polymerization of 1.9 mol/L solution of GM in CH_2Cl_2 at −20 °C with 1×10^{-3} mol/L of TFA is complete within 20 min. Propagation in GM polymerization, similar to polymerization of other aldehydes,[8] is a reversible reaction; the equilibrium monomer concentration is equal to 1.0 mol/L at 26 °C and to 0.06 at −30 °C.[7]

Homopolymerization of DXL initiated with TFA and its derivatives (esters and anhydride) has been studied extensively. Because of the equilibrium between ionic and covalent (less reactive) active species, the rates of polymerization are lower than those for initiators providing counterions unable to form covalent bonds (e.g., SbF_6^-), but they are still relatively high; thus at −15 °C, polymerization is complete in less than 3 h.[9] Propagation in DXL polymerization is also a reversible reaction; the equilibrium monomer concentration is equal to 2.0 mol/L at 26 °C and to 0.34 mol/L at −20 °C.[10]

Copolymerization of GM with DXL was therefore conducted in CH_2Cl_2 solution at temperatures below room temperature, with TFA as initiator.

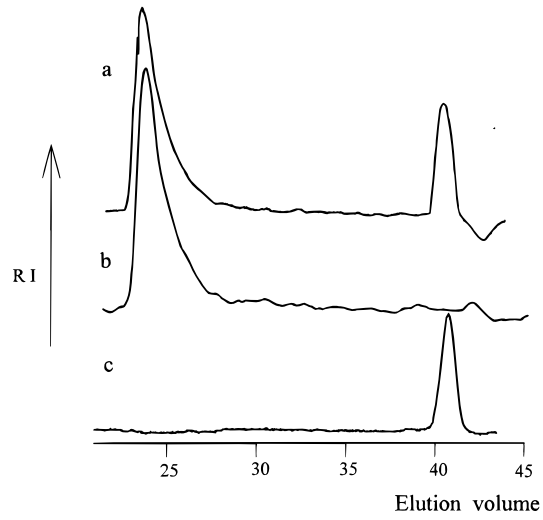


Figure 1. Typical GPC curves of the copolymerization mixture**.** Conditions: $[GM]_0 = 3.0$ mol/L, $[DXL]_0 = 6.0$ mol/L, and $[CF_3SO_3H]_0 = 4.30 \times 10^{-3}$ mol/L; in CH_2Cl_2 at −30 °C. (a) crude product, (b) methanol-insoluble fraction, (c) methanol-soluble fraction.

Random Copolymerization of Methyl Glyoxolate with 1,3-Dioxolane. Copolymerization of GM with DXL was studied in the following range of comonomer concentrations: $[GM]_0 = 1.6-4.8$ mol/L and $[DXL]_0 = 1.8-6.2$ mol/L. Conversions of both comonomers were close to quantitative (>90% mol.). Thus, for example, at $[GM]_0 = 1.6$ mol/L, $[DXL]_0 = 6.2$ mol/L, and $[TfOH]_0 = 6.5 \times 10^{-3}$ mol/L in CH_2Cl_2 solution at −30° after 15 min, conversion of GM was practically equal to 100%, and conversion of DXL was equal to 92%. The degree of conversion was determined from ^{1}H NMR spectra of reaction mixtures.

In all cases, analyses of the GPC curves of the reaction products indicate the presence of two fractions. A typical GPC curve is shown in Figure 1. In addition to the polymer fraction, a peak of the low-molar-mass component appears in all of the chromatograms at the same elution volume, independently of the molar mass of the polymer fraction. The polymer was separated from the low-molar-mass compound by precipitation from CH_2Cl_2 solution into methanol (taken in 5-fold excess). Parts b and c of Figure 1 show GPC curves of the precipitated polymer and of the soluble fraction (low-molar-mass compound). The results show that separation is practically quantitative for copolymers with $M_n > 6000$. Copolymers with lower M_n's are partly soluble in CH_2Cl_2/CH_3OH (1/5 v/v), and thus separation is not quantitative.

Analysis of the Low-Molar-Mass Product. The product soluble in the CH_2Cl_2/CH_3OH mixture (1/5 v/v) was distilled under vacuum. Fraction boiling at 86° at 15 mmHg was collected giving pure product (99.9% purity according to GLC). Figure 2 shows ^{1}H NMR spectrum of this fraction.

Analysis of the spectrum, coupled with results of the elemental analysis and mass spectroscopy (cf. Experimental Section) indicates that the product is a cyclic heterodimer, containing one GM and one DXL unit, as shown in Scheme 2.

In the ^{1}H NMR spectra of cyclic heterodimer (Figure 2), signals characteristic for the following groups appear: $-COOCH_3$ (e) (singlet at 3.81 ppm δ), $-OCH_2-CH_2O-$ (b) (multiplet at 4.10−4.14 ppm δ) and (b′ + c′

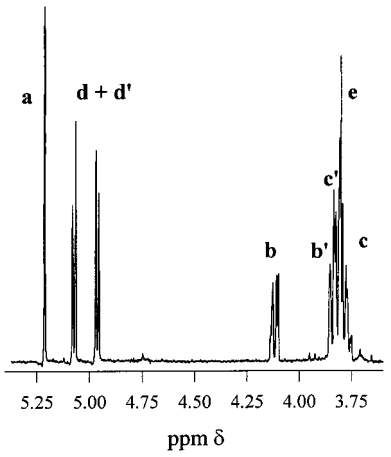
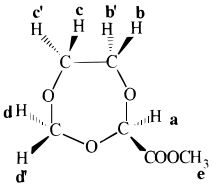


Figure 2. ^{1}H NMR spectrum of a cyclic heterodimer. Assignments given in the text.

Scheme 2



+ c) (multiplet at 3.77−3.86 ppm δ), $-OCH_2-$ (d + d′) (AB pattern with a center at 5.02 ppm δ), and $-OCHO-$ (a) (singlet at 5.21 ppm δ). The observed intensity ratio is equal to a:b:b′:c:c′:d:d′:e = 1:1.02:1.24:1.03:1.15:1.00:0.98:3.10 and is close to the expected ratio.

The cyclic heterodimer contains a center of chirality at the carbon atom of the GM unit. Protons of the $-OCH_2O-$ groups from DXL unit are thus magnetically non equivalent. Protons of this group appear, therefore, not as a singlet as in DXL repeating units in homopolymers but as four signals of a typical AB pattern. The same is true for protons of the $-OCHR-OCH_2CH_2O-$ group denoted as b and b′ in Scheme 2. This group is separated from the carbon atom constituting the center of chirality by one oxygen atom; in other words, it is in the same position with respect to the center of chirality as the $-OCH_2O-$ group. Consequently, protons b and b′ give also a series of signals. One fragment of the spectrum of protons b and b′ appears as the multiplet at 4.10−4.14 ppm δ, whereas the other one overlaps with signals of protons of the second methylene group in the $-OCHR-OCH_2CH_2O-$ group, giving a multiplet at 3.77−3.86 ppm δ.

In ^{13}C NMR spectra of cyclic heterodimer, the following signals appear: $-OCH_3$ (52.4 ppm δ), $-OCH_2CH_2-$ (69.5 ppm δ), $-OCH_2O-$ (91.6 ppm δ), $-CHO-$ (95.6 ppm δ), and $-C{=}O$ (167.5 ppm δ). 2D spectrum (correlation: $^1H-^{13}C$) confirms the proposed assignments of the ^{1}H NMR signals. The group of signals in the region 5.02 ppm δ (the center of AB pattern) in ^{1}H NMR spectra (protons of the $-OCH_2O-$ group) is correlated with the corresponding signal of a single carbon atom at 91.6 ppm δ. In addition, a group of signals at 4.10−4.14 and 3.71−3.86 ppm δ is correlated with a signal of the corresponding carbon atom at 69.5 ppm δ. Analyses of the 2D spectra confirm that in ^{1}H NMR spectrum signals of $-OCH_2CH_2O-$ and $-COOCH_3$ groups partly overlap in the region 3.7−3.9 ppm δ.

Formation of a Cyclic Heterodimer (CHD). Formation of cyclic oligomers is a general feature of cationic ring-opening polymerizations.[11] Cyclization proceeds as a backbiting (or endbiting) process, involving intramolecular nucleophilic attack of an oxygen atom of the own chain on the carbon atom in the growing species bearing partial positive charge.

Table 1. Change of Concentration of a Cyclic Dimer after Addition of New Portion of One of Comonomers (DXL)[a]

operation	$[DXL]_o$ mol/L	$[GM]_o$ mol/L	$[CF_3SO_3H]_o$ mol/L	$[dimer]_e$[b] mol/L
copolymerization	4.0	4.1	3.5×10^{-3}	2.6
addition of acid			8.4×10^{-3}	2.7
addition of DXL and acid	5.2		2.9×10^{-2}	1.7

[a] In CH_2Cl_2 at −30 °C [b] Corrected for volume changes and related to the initial volume of the reaction mixture.

Formation of the low-molar-mass cyclic oligomers is facilitated if cyclic compounds with low ring strain can be formed.[12] In some polymerizations, formation of the low-molar-mass cyclic oligomers may be a reversible process. Thus, cyclic oligomer is formed until its concentration reaches an equilibrium concentration.[11] The situation may became more complex in copolymerization; the proportions of both comonomers in feed and the structure of copolymer formed may change during the process. Thus, the equilibrium concentration of cyclic oligomer can change in the course of copolymerization.[13,14]

CHD is a substituted analogue of 1,3,5-trioxepane (cyclic dimer of DXL and formaldehyde) known to undergo reversible homopolymerization.[15,16]

To establish the reversibility of CHD formation its ability to undergo copolymerization with DXL was investigated in an "in situ" system, without isolation of CHD.Thus, GM was copolymerized with DXL under typical conditions shown in Table 1. After 15 min, a sample of the reaction mixture was withdrawn and analyzed. The reaction mixture contained linear copolymer and CHD, in proportions shown in Table 1. To the remaining part of the reaction mixture, a new portion of initiator was added to confirm that the observed fractions of CHD and linear copolymer do correspond to the final (either kinetic or thermodynamic) distribution. As shown in Table 1, the distribution in sample 2 was the same as that in sample 1. This observation is already a strong indication that CHD is formed reversibly, in other words, that the observed CHD concentration is an equilibrium concentration governed by thermodynamics. The initial molar ratio of comonomers in the feed was equal to 1:1. If CHD is formed by a backbiting process, it requires the presence of the GM−DXL or DXL−GM heterodiads at the growing chain end. Polyacetal chains undergo fast transacetalization, leading to redistribution of the comonomer units. Therefore, for the 1:1 comonomer feed composition, transacetalization should continuously generate terminal heterodiads, until eventually the only product of the reaction were CHD, if its formation were irreversible. This was not observed, and the very fact that, after addition of initiator to the reaction mixture and retention of this mixture for a relatively long time, the concentration of CHD did not change shows that the system is already at equilibrium. This was confirmed by analysis of the composition of the reaction mixture after subsequent addition of new portions of an initiator and a DXL comonomer. The considerable decrease of the concentration of CHD in the system (after correction for a volume change) indicates that CHD was incorporated into the linear polymer by copolymerization with the newly

Table 2. Dependence of the Yield of Cyclic Dimer on the Composition of the Comonomer Feed[a]

$[GM]_o$ mol/L	$[DXL]_o$ mol/L	$[CF_3SO_3H]_o$ $\times 10^3$ mol/L	wt % cyclic frac.
4.8	1.8	3.8	16
5.9	3.0	1.4	27
3.6	3.6	4.3	68
3.0	6.0	4.3	25
1.6	6.2	6.5	21

[a] In CH_2Cl_2 at −30 °C

Scheme 3

GM + DXL ⇌ linear copolymer ⇌ mixed cyclic dimer

added DXL. In terms of monomer−polymer equilibrium, it means that the new equilibrium CHD concentration (in equilibrium with polymers enriched with DXL units) was reached.

Thus, the results shown in Table 1 provide proof that formation of CHD is an reversible process and that the final concentration of CHD is governed by thermodynamics.

As already indicated, formation of CHD by backbiting requires the presence of the GM−DXL (or DXL−GM) heterodiad at the growing chain end. The probability of formation of such heterodiads is higher the closer the system comes to the 1:1 molar ratio of comonomers.

To confirm that the CHD yield depends on the composition of the comonomer feed, the final yield of CHD was determined in a series of experiments performed with different molar ratios of comonomers in the feed. Results are collected in Table 2.

According to Table 2, the yield of CHD is indeed the highest for equimolar mixture of comonomers, and it decreases with increasing proportions of either of the two comonomers.

Formation of cyclic oligomers in the cationic homopolymerization of DXL was studied and discussed in detail.[17−19] It was shown that the cyclic fraction contains mainly higher cyclic oligomers containing at least 25 atoms in the ring (cyclic pentamers and higher). The distribution of these higher cyclic oligomers conforms to the Jacobson−Stockmayer theory.[20] Lower cyclic oligomers are formed in negligible quantities, due to the fact that such rings are still strained.

No cyclic oligomers have been detected until now in the cationic homopolymerization of GM.

When GM is copolymerized with DXL, cyclization is favored by the fact that a lower strain seven-membered ring, containing only one bulky substituent, may be formed.

The complete scheme of copolymerization can be visualized as shown in Scheme 3.

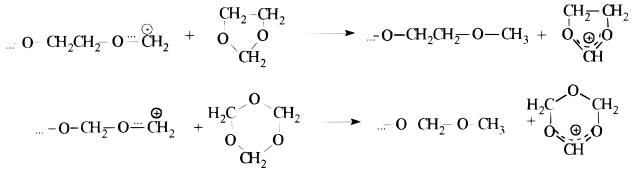
Molar Mass of Linear Copolymers. Cationic homopolymerization of DXL is known to proceed, under kinetically controlled conditions, without appreciable transfer or termination. Polymers with polymerization degrees equal to the values calculated for living polymerization as $DP_n = ([M]_0 - [M]_e)/[I]_0$ were obtained (these ratios were corrected for the formation of a cyclic fraction).[9,21] Cationic homopolymerization of GM leads, however, to polymers with $DP_n < 50$, even for much higher $[M]_0/[I]_0$ ratios.[6] Apparently, chain transfer operates, although the exact nature of this reaction has not been established yet. It may be thus expected that the extent of chain transfer is related to the composition of copolymer, which in turn depends on the composition

Table 3. Dependence of Molecular Weights of Copolymers on the Comonomers Feed Composition[a]

$[GM]_o$ mol/L	$[DXL]_o$ mol/L	$[I]_o$ $\times 10^3$ mol/L	M_n found[b]	M_n found/M_n calcd	[−DXL−] in copolym.
4.8	1.8	3.8	3400	0.02	0.29
5.9	3.0	1.4	6650	0.02	0.32
3.6	3.6	4.3	3400	0.03	0.63
3.0	6.0	4.3	17500	0.17	0.76
1.6	6.2	6.5	16900	0.27	0.87

[a] In CF_3SO_3H and CH_2Cl_2 at −30 °C. [b] Determined by GPC.

Scheme 4



In cationic polymerization of cyclic acetals (and possibly aldehydes) an equilibrium exists between carboxonium and oxonium ions. Although they may differ in reactivity, both lead to the same reaction products.
For simplity, in this and in the following schemes, only carboxonium ion form of active species is shown, counterions are omitted.

of the comonomer feed. This is indeed the case, as shown by the data of Table 3.

In all cases, M_n is considerably lower than the value calculated for a living process. The number-average molar mass of the copolymer increases with increasing $[DXL]_0/[GM]_0$ ratio, indicating that GM is chiefly responsible for transfer.

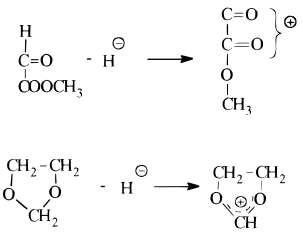
A typical chain-transfer reaction occurring in the polymerization of heterocyclic monomers (including cyclic acetals) is intra- or intermolecular chain transfer to polymer. Intermolecular reaction, however, does not affect the M_n values, the only consequence being broadening of the molar mass distribution.[22] Intramolecular chain transfer leads to some decrease of M_n values of the linear fraction, due to the splitting off of cyclic oligomers.

In systems in which carboxonium-active species coexist with tertiary oxonium-active species, in significant proportions, another possibility exists, namely, hydride ion transfer, which has been shown to operate, although inefficiently, in cationic polymerization of 1,3-dioxolane[23] and 1,3,5-trioxane (formaldehyde trimer).[24]

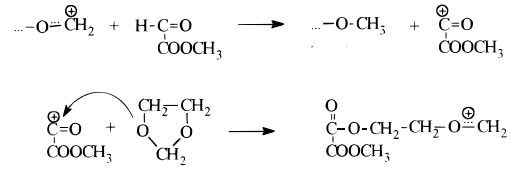
1,3-Dioxolane-2-ylium or 1,3,5-trioxane-2-ylium cations are formed, respectively, and they initiate the new chain;[25] consequently the reaction shown in Scheme 4 leads to the lowering of M_n.

In the cationic copolymerization of DXL with GM, there are two potential hydride ion donors (monomers) and two potential hydride ion acceptors (carboxonium ions derived from terminal DXL or GM unit). From the two comonomers, the better hydride ion donor should be the one that gives the more stabilized carboxonium ion. Stabilization is more efficient in the case of carboxonium ion derived from GM; besides, DXL is known to be a relatively poor hydride ion donor[23] (see Scheme 5). On the other hand, the more stable carboxonium ion should be the less effective hydride ion acceptor; consequently, the more active hydride ion acceptor should be the carboxonium ion derived from a DXL terminal unit. The prevailing reaction should therefore be the hydride ion transfer from the GM molecule (a better hydride ion donor) to the $-DXL^+$ active species (a more active hydride ion acceptor); see Scheme 6. The proposed reaction scheme should lead to macromolecules contain-

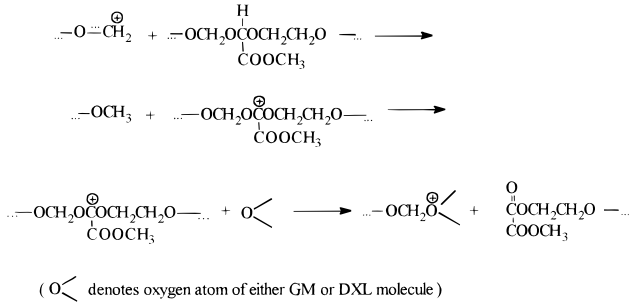
Scheme 5



Scheme 6



Scheme 7



(O< denotes oxygen atom of either GM or DXL molecule)

ing methoxy and oxalate ester end groups. The signals of protons of the oxalate ester groups, $CH_3OCOCOOCH_2$-CH_2O- in ^1H NMR, should, according to the literature, appear at the 4,1−4.4 ppm δ region.[26] In ^1H NMR of the isolated and reprecipitated copolymer, a multiplet is indeed observed in this region. The signals of the $-OCH_3$ groups at 3.4−3.5 ppm δ region are also present in the spectra, indicating that the chain-transfer reaction proceeds according to the proposed scheme.

It should be noted that the same effect would be observed if hydride transfer proceeded not from the GM monomer but from a GM repeating unit of the copolymer. As shown in Scheme 7, scission of the resulting polymeric carboxonium ion would lead to a decrease of M_n values and formation of the same end groups as in the reaction proceeding by the previous scheme. These two possibilities cannot therefore be distinguished by analytical methods.

There are also further indications that the hydride-transfer reaction may be followed by reaction of a newly formed carboxonium ion with a polymer chain. In an attempted synthesis of block copolymers by sequential polymerization in which living poly-DXL prepared in an initial stage was used to initiate the polymerization of GM, the isolated products had molar masses considerably lower than the molar mass of the starting living poly-DXL. Results are collected in Table 4.

Again, as in random copolymerization, the molar mass decrease is especially pronounced for copolymers with higher content of the GM units, which confirms that hydride transfer proceeds predominantly from the GM unit; see Scheme 8. Chain transfer may be to some extent limited by decreasing temperature, because typically, in cationic polymerization, the activation energy for chain-transfer reactions is higher than the activation energy for propagation. However, even at −78 °C, the M_n values are considerably lower than those calculated for a living system. (Table 5).

Table 4. Molar Masses of Copolymers Resulting from Attempted Sequential Copolymerization[a]

$[GM]_0/[-DXL-]$	M_n of starting poly-DXL	M_n of copolymer
2.5/1	13 400	2 300
1.6/1	4 300	2 400
1/3	36 000	25 000

[a] GM added to living solution of poly-DXL. Experiments were carried out in CF_3SO_3H and CH_2Cl_2 at −78 °C

Scheme 8

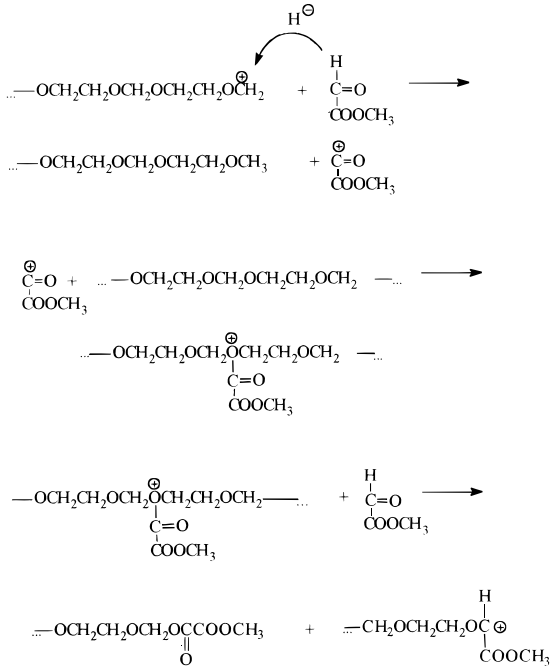


Table 5. Dependence of the Molar Masses of GM−DXL Copolymers on Temperature

system	temp. [°C]	M_n calcd for living system	M_n found	yield of copolym.[a]
$[I]_0 = 5.7 \times 10^{-3}$, $[GM]_0 = 3.2$, $[DXL]_0 = 3.4$	−78	93 000	9700	97
$[I]_0 = 5.7 \times 10^{-3}$, $[GM]_0 = 3.2$, $[DXL]_0 = 3.4$	−30	93 000	2300	98
$[I]_0 = 8.3 \times 10^{-4}$, $[GM]_0 = 1.5$, $[DXL]_0 = 3.1$	25	435 000	720	85

[a] In weight percent and with respect to sum of comonomers

Copolymer Composition. The copolymer composition was determined by ^1H NMR. A typical ^1H NMR spectrum is shown in Figure 3.

The ^1H NMR spectrum of poly-DXL is well-known; it consists of two singlets corresponding to protons of $-OCH_2O-$ groups at 4.74 ppm δ and protons of $-OCH_2$-CH_2- groups at 3.74 ppm δ, respectively. The spectra of homopoly-GM are more complex, owing the presence of the center of chirality in the GM repeating unit. The sequences with different tacticities give a complex pattern for the signal of protons of −CHO− groups at the region 5.6−5.8 ppm δ, whereas the signal of protons of the $-COOCH_3$ groups, separated from the center of chirality by four bonds, is not resolved into components,

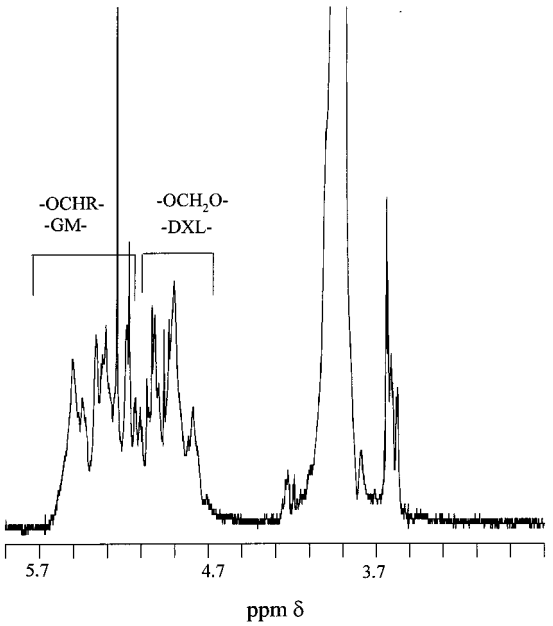


Figure 3. ^{1}H NMR spectrum of the GM−DXL copolymer ([−GM−]/[−DXL−] = 0.71/0.29). Assignments given in the text.

because of the different tacticities; it appears as a broad signal at 3.81 ppm δ.[27]

The spectra of copolymers are still more complex, because chemical shifts may be affected by both tacticity and the sequence of repeating units in copolymers. The spectra become simpler for copolymers with a higher proportion of DXL units, provided the probability of forming longer GM sequences is low. If GM units are separated by at least one DXL unit (five bonds), the centers of chirality are sufficiently far away one from another and the effect of tacticity is considerably reduced. Even then, however, as shown in Figure 3, the signal of protons of the −CHO− groups of the GM units appear as an irregular multiplet in the region of 5.1−5.7 ppm δ.

Signals corresponding to $-OCH_2O-$ and $-OCH_2CH_2O-$ groups from DXL unit give also a rather complex pattern. For a DXL unit flanked by two other DXL units, the chemical shifts should be close to those observed for homopolymers, and signals with chemical shifts equal to 4.75 and 3.71 ppm δ indeed appear in the spectra of copolymers. These signals have therefore been assigned to $-OCH_2O-$ and $-OCH_2CH_2O-$ groups in central DXL unit in a DXL homotriad (or longer sequence). In a DXL unit followed by the GM units, protons of the $-OCH_2O-$ group are becoming magnetically nonequivalent and give a characteristic AB pattern in the region 4.8−5.1 ppm δ, as in a cyclic heterodimer. Similarly, the protons of the $-OCH_2CH_2O-$ group are not equivalent, giving a multiplet at 3.71−3.82 ppm δ.

The overall composition of copolymers can therefore be determined by comparing the intensity of the signals at the 5.1−5.7 (−OCHO− group from GM unit) and 4.74−5.10 ppm δ regions ($-OCH_2O-$ group from DXL unit).

Copolymer Microstructure. The compositional microstructure of copolymers (distribution of the comonomer repeating units within the chain) is usually determined by analysis of the ^{13}C NMR spectra. ^{13}C NMR spectra of the DXL−GM copolymers are difficult to analyze because, at higher proportion of the DXL units,

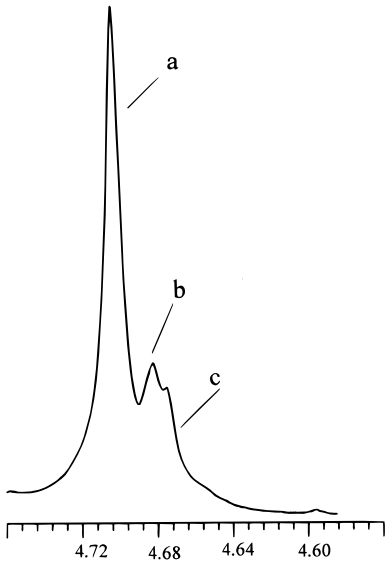
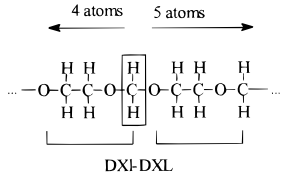


Figure 4. ^{1}H NMR spectrum of the GM−DXL copolymer. Expanded region of absorption of the $-OCH_2O-$ groups in the DXL−DXL homodiads. (a) $-OCH_2CH_2O\mathit{CH_2}-OCH_2CH_2OCH_2-$ in the DXL−DXL diad flanked by two DXL units (DXL−DXL−DXL−DXL tetrad), (b) $-OCH_2CH_2O\mathit{CH_2}-OCH_2CH_2OCH_2-$ in the DXL−DXL diad flanked by one DXL and one GM unit (DXL−DXL−DXL−GM tetrad), and (c) $-OCH_2CH_2O\mathit{CH_2}-OCH_2CH_2OCH_2-$ in the DXL−DXL diad flanked by two GM units (GM−DXL−DXL−GM tetrad).

Scheme 9



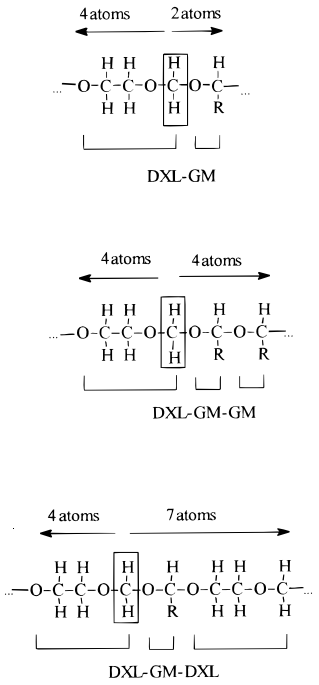
signals corresponding to different sequences are not sufficiently well separated; at higher proportion of GM units, the spectra are complicated by differences in tacticity of longer GM sequences. Therefore, the microstructure of copolymers was determined by analyzing the ^{1}H NMR spectra.

For the $-OCH_2O-$ groups of the DXL units, signals at about 4.7 ppm δ, assigned to the DXL−DXL homodiad, and signals at 4.8−5.1 ppm δ, assigned to the DXL−GM heterodiad, are observed. The signal corresponding to the homodiad is split into a few lines, which means that the chemical shift is affected by the nature of the repeating units flanking the DXL−DXL diad. The group under consideration (cf. Scheme 9) is located almost in the middle of the DXL−DXL homodiad.

Thus, its chemical shift should be affected to the same degree by the nature of the repeating units from both sides of the DXL−DXL diad. In other words, splitting of the signal of the $-OCH_2O-$ group in a given homodiad means that the chemical shift is sensitive to the nature of tetrads, of which the homodiad is the central block. It was assumed, that the most dissimilar tetrads, DXL−DXL−DXL−DXL and GM−DXL−DXL−GM, give signals at both sides of a multiplet, whereas signals corresponding to the tetrads, DXL−DXL−DXL−GM and GM−DXL−DXL−DXL, overlap, giving one line in between. The assignments are shown in Figure 4.

The acetal group ($-O-CH_2-O-$) in the DXL−GM heterodiad is not located in the middle of the heterodiad. Because the effects of the neighboring units are trans-

Scheme 10



ferred mainly through the chain, these effects depend on the distance (i.e., number of connecting bonds) between the group under consideration and the neighboring units; see Scheme 10. The GM units introduce two atoms into the chain, whereas DXL units introduce five atoms. Therefore, the distance between the $-OCH_2O-$ group and the right-hand side neighbor will be the same for the DXL−GM−GM triad as for the DXL−DXL diad. Thus, the chemical shift of the $-OCH_2O-$ group will be affected to the same degree by the nature of both flanking groups; in other words, the signal corresponding to the DXL−GM−GM should be further split into signals of the corresponding pentads. The situation is, however, different, for the other triad derived from the DXL−GM diad, namely, the DXL−GM−DXL triad. In this case (cf. Scheme 10), the left-hand side neighboring unit flanking the triad is much closer to the $-OCH_2O-$ group than the right-hand side neighboring unit. It may happen that only the nature of the first one will influence the chemical shift, and the sequence of tetrads would be observed. In copolymerization of vinyl monomers, when the comonomers contribute two atoms to the chain, structural information concerning either only odd (triads, pentads) or only even (diads, tetrads) sequences may be obtained from the spectra. In the present system, on the contrary, at least some signals may be sensitive to the nature of both odd and even sequences, which makes the spectra much more complex.

Thus, the analysis of the sequence distribution was limited to diads. In a random copolymer, the fraction of homo- and heterodiads is given by the Bernoullian statistics;[28] see Scheme 11.In Table 6, the observed fractions of the DXL−DXL homodiads and the DXL−GM heterodiads are compared with the values calculated for random copolymers.

The observed fractions of the DXL−DXL homodiads are in all cases lower than those calculated for random copolymer, and this effect is more pronounced for higher ratios of [−GM−]/[−DXL−] repeating units. Random copolymers are formed when the product of comonomer

Scheme 11

$$m_1m_1 = \frac{m_1^2}{(m_1 + m_2)^2}$$

$$m_1m_2 = \frac{m_1 \times m_2}{(m_1 + m_2)^2}$$

Where : m_1m_1 - mol fraction of DXL-DXL homodiads in copolymer
m_1m_2 - mol fraction of DXL-GM heterodiads in copolymer
m_1 - mol fraction of DXL units in copolymer
m_2 - mol fraction of GM units in copolymer

Table 6. Content of DXL−DXL Homodiads in GM−DXL Copolymers Prepared by Statistical Copolymerization[a]

compos. of copolym. [DXL]	[DXL−DXL] / [DXL−DXL] + [DXL−GM] calcd for random copolym	[DXL−DXL] / [DXL−DXL] + [DXL−GM] determd
0.87	0.87	0.73
0.76	0.76	0.55
0.63	0.63	0.31
0.32	0.32	0.18
0.29	0.29	0.19

[a]The values calculated according to the equations of Scheme 11 are compared with the values determined from analysis of ^{1}H NMR spectra. Experiments were carried out in CF_3SO_3H and CH_2Cl_2 at −30 °C.

reactivity ratios is equal to one ($r_1r_2 = 1$). Random copolymers may, however, result also from subsequent redistribution of repeating units in the initially formed (not necessarily random) copolymer. It is well-known that polyacetals readily undergo transacetalization, leading to redistribution of repeating units; this process is sometimes called “scrambling” or “reshuffling”.[29] To confirm that scrambling indeed occurs in the studied system, the microstructure of copolymers formed by sequential copolymerization was studied. Results of the copolymer analysis are shown in Table 7.

Block copolymers, expected to be formed by sequential copolymerization, should contain homoblocks. In terms of diads, mostly DXL−DXL and GM−GM homodiads should be formed, with heterodiads appearing only at the junction between blocks. In the analyzed samples, however, the fractions of the corresponding diads are essentially the same as those in a random copolymer obtained by copolymerization of a mixture of comonomers. This indicates that transacetalization proceeds quickly in comparison with propagation, and the microstructure of the isolated copolymers is not governed by the kinetics of copolymerization but by transacetalization, which, independently of the mechanism of the copolymer formation (i.e., r_1 and r_2 values), eventually leads to the formation of a random copolymer.

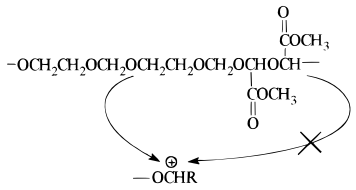
Transacetalization may also explain why in the isolated copolymers the content of the DXL−DXL homodiads is lower than that calculated for completely random copolymer. Transacetalization proceeds by an attack of the oxygen atom of the chain on the carbon atom in the growing species bearing a partially positive charge. Such an attack should proceed easier for an oxygen atom in the center of the DXL−DXL homodiad than for the oxygen atom vicinal to the GM unit, because of the steric hindrance resulting from the presence of a large substituent at the GM unit, as shown in the Scheme 12.For such a system, determination of the reactivity ratios (r_1 and r_2) is not possible, because the copolymer composition is not governed by the original rate constants of homo- and cross-propagation.

Table 7. Content of DXL−DXL Homodiads in GM−DXL Copolymers Resulting from Attempted Sequential Copolymerization[a]

$\frac{[DXL]}{[DXL]+[GM]}$ in copolymer	$\frac{[DXL-DXL]}{[DXL-DXL]+[DXL-GM]}$ calcd for random copolym.	$\frac{[DXL-DXL]}{[DXL-DXL]+[DXL-GM]}$ determd
0.75	0.76	0.69
0.32	0.32	0.09

[a] The values calculated according to the equations in Scheme 11 are compared with the values determined from analysis of ^{1}H NMR spectra. Experiments were carried out in CF_3SO_3H and CH_2Cl_2 at −30 °C.

Scheme 12



(R = H or $COOCH_3$)

Conclusions

It has been shown that an aldehyde, methyl glyoxylate, undergoes cationic copolymerization with a cyclic acetal, 1,3-dioxolane. The resulting copolymer is a polyacetal containing functional (ester) side groups. Copolymerization proceeds to nearly quantitative conversion of both comonomers, within a broad range of comonomer feed compositions. In all cases, copolymers with random distribution of comonomer sequences are isolated. Even when the copolymerization is carried out in a sequential mode, in other words, poly-DXL block is formed first and used to initiate polymerization of GM, a random copolymer is isolated instead of an expected block copolymer. Such behavior was observed earlier for the cationic copolymerization of two cyclic acetals, namely, 1,3-dioxolane and 1,3-dioxepane, and it was explained by participation of transacetalization reaction being at least as fast as propagation.[9]

Results of the studies of model systems indicate[30] that transacetalization under conditions of cationic polymerization of cyclic acetals proceeds fast enough to compete effectively with propagation. Because intermolecular transacetalization (scrambling) leads to redistribution of the comonomer units in copolymer at any stage of copolymerization, a random and uniform copolymer is isolated at nearly quantitative conversion of both comonomers. Thus, the distribution of comonomer units in copolymers is not governed by the kinetics of propagation but by the kinetics of randomization resulting from chain transfer to polymer followed by chain scission.

Fast intramolecular reaction leads to an equilibrium between linear copolymer and cyclic oligomer(s). In the system studied, the cyclic heterodimer (CHD) was the only cyclic oligomer detected, which indicates that this particular cyclic oligomer is formed preferentially.

The contribution of intramolecular transacetalization (cyclization) is a disadvantage from the synthetic point of view, because, in addition to the linear copolymer (desired product), a significant amount of low-molar-mass cyclic oligomer (CHD) is formed. The amount of CHD may however be reduced by using a large excess of one of the comonomers.

The contribution of intermolecular transacetalization (scrambling) on one hand precludes the formation of block copolymer in sequential copolymerization but, on the other hand, leads to the formation of a random copolymer, independently of the kinetic conditions. Typically, in a copolymerization, one of the comonomers is consumed faster that the other one, and chains (or chain segments) formed at the early and late stages of copolymerization may differ significantly in composition and microstructure. In the system studied, intermolecular transacetalization leads to uniform random distribution of comonomer sequences, independently of the "kinetic history" of the system. This is a significant advantage, because it leads to uniform distribution of functional side groups along the polymer chain.

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