Poly(2,4-hexadiyn-1,6-ylene carbonate). Synthesis and Topochemical Cross-Linking Reaction

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ABSTRACT: Poly(2,4-hexadiyn-1,6-ylene carbonate) (**2**) was prepared by dehydropolycondensation of dipropargyl carbonate. The polycarbonate with conjugated diacetylene units in the backbone was cross-linked by photochemical and thermal treatment (in the sense of a topochemical reaction) and compared with the structurally similar polyesters **4a** and **4b**. The photochemical and thermal cross-linking was followed by UV spectroscopy. Finally a time–conversion diagram of the thermal cross-linking was established. The cross-linked polycarbonate **2** is a shock- and heat-sensitive polymer. Precautions in handling this cross-linked polymer should be observed since explosions may occur.

Introduction

Polyesters containing conjugated diacetylene groups in the backbone were first described by Wegner[1] and later by Patil.[2] They obtained crystalline polymers in a Schotten–Baumann type reaction, starting from 2,4-hexadiyne-1,6-diol and diacid chlorides of dicarboxylic acids. The diacetylene unit was incorporated also in polyurethanes and aromatic polyethers,[3-5] on the one hand by a polyaddition reaction of 2,4-hexadiyne-1,6-diol to α,ω-diisocyanates[1-4] and on the other by an oxidative dehydropolycondensation of α,ω-diynylurethanes in pyridine solution with cupric chloride.[5] These polymers develop a deep red color on exposure to UV light or on heating below their melting point. During this process the polymers become insoluble; this is explained by a topochemical cross-linking reaction in the crystalline regions of the polymer.

The most detailed study of the synthesis and topochemical polymerization of conjugated diacetylenes was carried out with poly(1,11-dodecadiyne) and related polymers of the general structure $[C{\equiv}CC{\equiv}C(CH_2)_n]_x$.[6-9] The synthesis of these polymers containing diyne groups and hydrocarbon chain segments was achieved via oxidative coupling of α,ω-diyne monomers with a copper–pyridine catalyst. The cross-linking reaction of these polymers showed a dependence on the length of the hydrocarbon chain segment; i.e., the polymers with $n = 5$ and 8 may be cross-linked by UV or higher energy radiation, while the polymer with $n = 6$ is not cross-linked. The structures of poly(1,11-dodecadiyne) were studied by solid-state high-resolution ^{13}C NMR spectroscopy,[9] by electron diffraction,[7] and by X-ray diffraction techniques[6] before and after cross-linking in order to obtain some information on the mechanism of cross-linking. The chromic behavior of cross-polymerized poly(1,8-nonadiyne) was studied by means of optical spectroscopy and resonance Raman spectroscopy.[8]

In the present paper we report on the results of our investigations regarding the behavior of polyesters with conjugated diacetylene moieties in the main chain of the type $-R_xCOOCH_2C{\equiv}CC{\equiv}CCH_2-$ as a function of the spacer R_x. Further, the synthesis and properties of a new polymer, poly(2,4-hexadiyn-1,6-ylene carbonate) (R_x = O), are presented and compared with the known polyesters of adipic [$R_x = OCO(CH_2)_4$] and sebacic acid [$R_x = OCO(CH_2)_8$] containing the same diol. The mechanistic interpretation of the cross-linking was done in parallel to the literature (e.g., ref 2). Since it turned out that poly(2,4-hexadiyn-1,6-ylene carbonate) decomposes explosively under certain circumstances, the analytical methods that can be applied are limited.

Experimental Section

Reagents. Diphenyl carbonate (from Bayer AG), adipic acid chloride, sebacic acid chloride (from Merck), and propargyl alcohol (from Fluka) were used without any purification for the synthesis of the monomers **1**, **3a**, and **3b** (Chart I). All solvents used were of p.A. grade and were distilled and dried before use. The oxidation catalyst, cuprous chloride/TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) (from Merck), for the Glaser coupling reaction was prepared in situ in the corresponding solvent (acetone, tetrahydrofuran, or dimethyl sulfoxide). The purification of the polymer was performed with silica gel 60, 230–400 mesh (from Merck).

Monomer Synthesis. Dipropargyl carbonate (**1**) was prepared by transesterification of diphenyl carbonate with propargyl alcohol (used also as the solvent) with sodium methoxide as catalyst. Dipropargyl adipate and sebacate were prepared via Schotten–Baumann reaction from the corresponding acid chlorides in diethyl ether as solvent and propargyl alcohol. Pyridine was used for the neutralization of the resulting hydrochloric acid. The monomers were purified by distillation.

Polymerization Procedure. A solution of 0.01 mol of cuprous chloride and 0.01 mol of TMEDA in 150 mL of solvent (acetone, tetrahydrofuran, or dimethyl sulfoxide) was heated to 35 °C, and oxygen was introduced into the solution and dispersed with a vibromixer. To the blue solution was added 0.1 mol of monomer (**1**, **3a**, or **3b**) dropwise, while the color changed to green. After 45 min the reappearance of a blue color indicated the end of the reaction. The reaction mixture was acidified with hydrochloric acid and passed over a column packed with 15 g of silica gel. The polymer solution was concentrated and the polymer precipitated in methanol. The polymer yield was 85%.

Topochemical Cross-Linking. Thin films of the polycarbonate **2** as well as of the polyesters **4a** and **4b** were cast on a quartz plate from methylene chloride solution and illuminated with a high-pressure mercury lamp. All materials were crystalline. For a kinetic study of the reaction a light source of 8-W was used at a wavelength of 254 nm and a distance of 25 cm between light source and sample. Thermal cross-linking was performed at 75 °C. For a time-conversion curve of the cross-linking reaction the amount of insoluble material in percent was determined at selected time intervals. All reactions were performed in air. The amount of insoluble material was determined by treatment of the processed material with methylene chloride (1:100 by weight) and isolation of the insoluble part by centrifugation, followed by quantitative determination.

Measurements. IR spectra were measured with a Perkin-Elmer 283 B spectrometer or a Nicolet FTIR 20 SXB spectrometer.

UV spectra were measured with a Perkin-Elmer 554 UV/vis spectrometer.

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Table I
Selected Data on Poly(2,4-hexadiyn-1,6-ylene carbonate) (2), Poly(2,4-hexadiyn-1,6-ylene adipate) (4a), and Poly(2,4-hexadiyn-1,6-ylene sebacate) (4b)

	2[16]	4a	4b
yield, %	85	85	90
feature	yellow-orange powder	yellow-orange powder	yellow powder
mol wt (GPC)[a]	5500	6600	8000
degree of polym (GPC)[a]	40	30	29
UV (film) absorpn max, nm	231, 244, 258	232, 245, 258	232, 244, 258
IR (film) absorpn bands, cm^{-1}	1760 (C=O), 1260 (C–O)	2940 (C–H), 1770 (C=O), 1140 (C–O)	2940 (C–H), 1760 (C=O), 1155 (C–O)
^{1}H NMR reson, ppm	4.81 (s, 4 H)	4.65 (s, 4 H), 2.36 (m, 4 H), 1.67 (m, 4 H)	4.64 (s, 4 H), 2.32 (t, 4 H), 1.60 (m, 4 H), 1.28 (m, 8 H)
^{13}C NMR reson, ppm	56.09 (C_ϵ), 71.28 (C_2), 73.04 (C_1), 153.70 (C_3)[b]	24.09 (C_β), 33.42 (C_α), 52.11 (C_ϵ), 70.26 (C_2), 73.67 (C_1), 172.06 (C_3)[c]	24.65 (C_δ), 28.70 ($C_{\beta,\gamma}$), 33.81 (C_α), 51.95 (C_ϵ), 70.15 (C_2), 73.66 (C_1), 172.62 (C_3)[d]
X-ray diffractn pattern, Å	3.3, 3.7, 4.0, 4.5, 9.0	3.3, 3.7, 4.0, 4.5, 8.0	3.3, 3.7, 4.0, 4.5, 10.9
degree of crystallinity, %	65	65	68
elem anal., %	calcd 61.77 (C), 2.96 (H) found 61.50 (C), 2.95 (H)	calcd 65.45 (C), 5.49 (H) found 64.88 (C), 5.61 (H)	calcd 69.55 (C), 7.30 (H) found 68.77 (C), 7.35 (H)
mp, °C	not determined	75	90

[a] Polystyrene standards. [b] $-OC_\epsilon C_1{\equiv}C_2C_2{\equiv}C_1C_\epsilon OC_3(O)-$. [c] $-C_3(O)C_\alpha C_\beta C_\beta C_\alpha C_3(O)OC_\epsilon C_1{\equiv}C_2C_2{\equiv}C_1C_\epsilon O-$. [d] $-C_3(O)C_\alpha C_\beta C_\gamma C_\delta C_\delta C_\gamma C_\beta C_\alpha C_3(O)OC_\epsilon C_1{\equiv}C_2C_2{\equiv}C_1C_\epsilon O-$.

Chart I

$HC{\equiv}CCH_2OCOOCH_2C{\equiv}CH$

1

$HC{\equiv}CCH_2O(COOCH_2C{\equiv}CC{\equiv}CCH_2O)_nCOOCH_2C{\equiv}CH$

2

$HC{\equiv}CCH_2OCO(CH_2)_xCOOCH_2C{\equiv}CH$

3a, $x = 4$
b, $x = 8$

$HC{\equiv}CCH_2O(OC(CH_2)_xCOOCH_2C{\equiv}CC{\equiv}CCH_2O)_nCO(CH_2)_xCOOCH_2C{\equiv}CH$

4a, $x = 4$
b, $x = 8$

^{1}H and ^{13}C NMR spectra were taken on a Bruker CXP spectrometer at 200 and 50.3 MHz, respectively, with deuteriochloroform as the solvent and TMS as the internal standard.

Elemental analyses were performed with a Carlo-Erba MOD 1106 instrument.

The X-ray diffraction powder patterns were recorded with an Iso-Debyeflex 1001 apparatus; a fine-structure X-ray tube (type SF 60) was used; Cu Kα = 1.54 Å; film–sample distance 39 mm.

GPC analyses were carried out by using a Waters apparatus with combined UV and RI detector. For the separation two columns were applied with PL gel (from Polymer Laboratories), 30-cm length, gel particle diameter 5 μm, and pore width 100 and 500 Å. THF was the eluting solvent with a flow rate of 1 mL/min.

Results and Discussion

There are two methods of choice for the synthesis of the title polymer: on the one hand, a Schotten–Baumann reaction of 2,4-hexadiyne-1,6-diol with phosgene and, on the other hand, an oxidative dehydropolycondensation of dipropargyl carbonate (**1**). The polymers should differ only by the end groups, which in the first case are hydroxyl and/or carboxyl groups and in the second case are acetylenic groups. We have chosen the oxydative dehdyropolycondensation for the synthesis of poly(2,4-hexadiyn-1,6-ylene carbonate) (**2**). In order to compare polymer **2** with chemically related polymers, we have chosen poly(2,4-hexadiyn-1,6-ylene adipate) (**4a**) and poly(2,4-hexadiyn-1,6-ylene sebacate) (**4b**) as reference polymers. In order to eliminate the influence of the end groups on the behavior of the polymer, **4a** and **4b** were prepared in the same manner as **2** starting from the corresponding propargyl esters **3a** and **3b** via dehydropolycondensation.

In the present paper the dehydropolycondensation reactions were carried out according to the method of Hay.[10] The terminal acetylene groups are converted to conjugated diynes with a catalyst system composed of cuprous chloride and TMEDA. The active coupling agent is prepared in situ via oxidation with molecular oxygen. The reaction mechanism for these dehydrocondensations proposed by Clifford and Waters[11] is generally accepted and has its validity also for polydehydrocondensation reactions. We applied this method to the α,ω-diacetylenes **1**, **3a**, and **3b** in order to obtain well-defined polymeric products. The optimum reaction temperature is between 25 and 45 °C. Below this temperature range no reaction takes place; above this temperature range, decomposition occurs, and a black product is obtained that could not be characterized. In the beginning the solution of the catalyst is heated to 35 °C in order to achieve a spontaneous initiation; afterward the heat of reaction must be removed by cooling the reaction mixture.

In Table I several data of polymers **2**, **4a**, and **4b** are summarized, which were used for further studies on photochemical and thermal cross-linking of the polymers. The yield of the polymer was always around 85% and independent of the solvent used (acetone, tetrahydrofuran, and dimethyl sulfoxide). All polymers were slightly colored powders, were soluble in tetrahydrofuran or halogenated hydrocarbons, and were capable of forming polymer films. The spectroscopic data as well as the elemental analyses are in agreement with the proposed structure. The GPC analyses indicate a relatively low molecular weight; the ^{1}H NMR spectrum of **2** does not allow detection of end groups, however. The acetylenic end groups can be detected for the oligomers of **2** at δ = 4.77 (d, J_{HH} = 2.5 Hz, 2 H) and δ = 2.53 (t, J_{HH} = 2.5 Hz, 1 H).

Since the crystallinity of the polymer samples is dependent on the sample preparation, all polymer samples were treated in the same way: column chromatography on silica gel and precipitation of the concentrated solution in methanol.

The powder X-ray diffraction patterns of polymers **2**, **4a**, and **4b** exhibit all sharp reflections, suggesting a high degree of crystallinity. As expected, the sample showed no difference in their X-ray diffraction patterns before and after cross-linking. It should be noticed that the spacers between the diacetylene groups seem to have no influence on the degree of crystallinity. The carbonate or ester function combined with the conjugated diacetylene

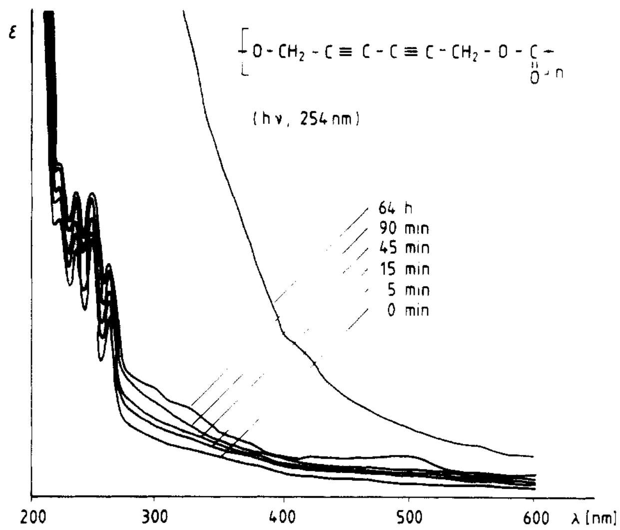

Figure 1. Absorption spectra of illuminated samples of poly(2,4-hexadiyn-1,6-ylene carbonate) (**2**) after selected exposure times. Experimental conditions: see the Experimental Section.

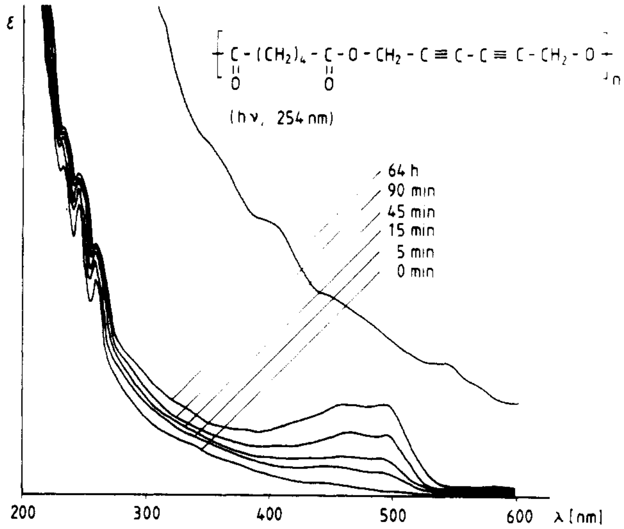

Figure 2. Absorption spectra of illuminated samples of poly(2,4-hexadiyn-1,6-ylene adipate) (**4a**) after selected exposure times. Experimental conditions: see the Experimental Section.

function obviously determines the crystallinity of the polymer. The degree of crystallinity was determined according to the method of Challa et al.[11,12]

Upon irradiation of thin films of polycarbonate **2** cast from methylene chloride on a quartz plate with a 200-W high-pressure mercury lamp, the films became red and after a short time the polymer became insoluble. In order to follow the course of the topochemical reaction we reduced the power of the light source to 8 W. Since the absorption bands of the diacetylene chromophore are at 232, 245, and 258 nm, we irradiated the samples with light of 254 nm. Figure 1 shows the absorption spectra of illuminated samples of **2** after selected exposure times. No significant changes can be observed in the region of 200–600 nm; besides that, the total absorption of the sample increases and covers the absorption region of the diacetylene chromophore.

The situation is different in the case of polymer samples **4a** and **4b** as can be seen from Figures 2 and 3. In the latter case, at the beginning of the reaction new broad absorption bands appear with maxima at 458 and 493 nm for **4a** and 461 and 495 nm for **4b**. A defined trend is observed: with an increasing number of the methylene groups, the intensity of the absorption bands increases.

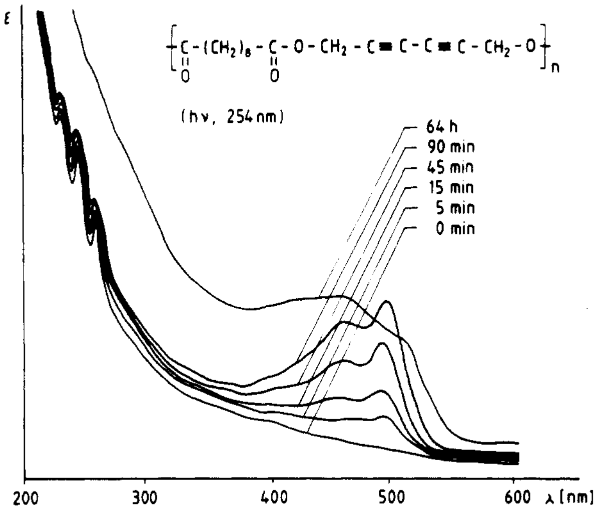

Figure 3. Absorption spectra of illuminated samples of poly(2,4-hexadiyn-1,6-ylene sebacate) (**4b**) after selected exposure times. Experimental conditions: see the Experimental Section.

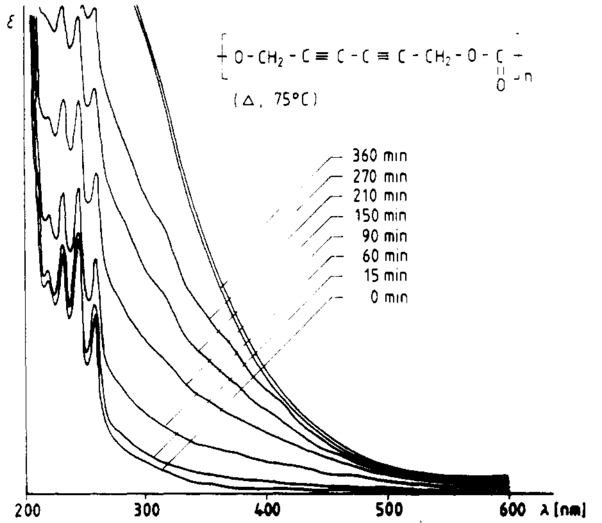

Figure 4. Absorption spectra of heated samples of poly(2,4-hexadiyn-1,6-ylene carbonate) (**2**), after selected exposure times. Experimental conditions: see the Experimental Section.

When samples of **2** are heated below the melting point, at 75 °C the polymer becomes colored and insoluble. Time-dependent UV spectral analyses of samples of polymers **2** and **4a** (Figures 4 and 5) revealed a behavior analogous to the case of the photochemical cross-linking; in the case of polymer **4a**, however, no new absorption bands appeared at 458 and 493 nm. For polycarbonate **2** and polyester **4a** a correlation between the degree of cross-linking and reaction time was established. As can be seen from Figure 6, polycarbonate **2** is cross-linked much faster than polyester **4a**. The cross-linking reaction of conjugated low molecular weight polymers shows in many cases an induction period,[13,14] which is a well-known kinetic effect. For the polycarbonate **2** and polyadipate **4a**, however, no induction period could be observed for the topochemical cross-linking. For the discontinuance of the polycarbonate curve experimental inaccuracy and not physical reasons are responsible. It should by noticed that the presence of all insoluble material does not mean 100% reaction of diacetylene groups. Fifty percent or less reaction could render everything insoluble.

Upon thermal cross-linking of polycarbonate **2** we observed that at higher temperatures (85 °C) an explosive decomposition of the polycarbonate occurs. Upon cross-linking polyesters **4a** and **4b** such a behavior was not

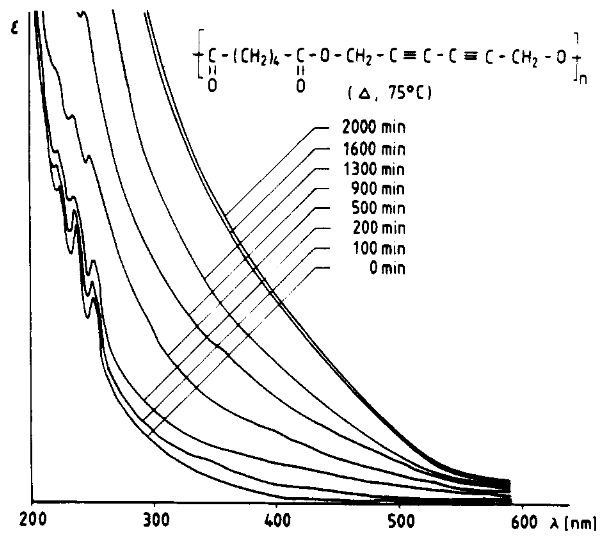

Figure 5. Absorption spectra of heated samples of poly(2,4-hexadiyn-1,6-ylene carbonate) (**4a**) after selected exposure times. Experimental conditions: see the Experimental Section.

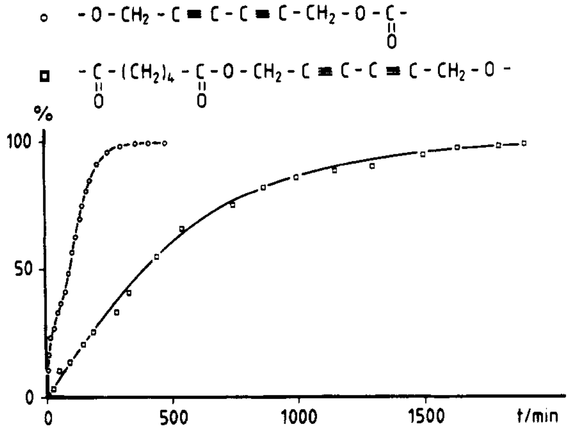

Figure 6. Time-conversion curve of the thermal cross-linking of (○) poly(2,4-hexadiyn-1,6-ylene carbonate) (**2**) and (□) poly(2,4-hexadiyn-1,6-ylene adipate) (**4a**).

Table II
Elemental Analysis (%) of Polymers 2, 4a, and 4b and of Their Thermally Cross-Linked Products in Air and under Nitrogen

	not cross-linked		cross-linked in air		cross-linked in N_2	
sample	C	H	C	H	C	H
2	61.50	2.95	58.80	2.90		
4a	64.88	5.75	60.40	5.46	64.90	5.76
4b	68.77	7.35	66.40	7.23		

observed, and from the literature no observation of this kind has been reported to the best of our knowledge.

In order to examine the reasons for the explosive decomposition of the polycarbonate, samples of **2**, **4a**, and **4b** were cross-linked in air and under nitrogen and subsequently analyzed (elemental analysis). Table II summarizes the results. The content of oxygen increases when the polymer samples are cross-linked in the presence of oxygen. For polycarbonate **2** the above data show that one oxygen atom is incorporated per three repeating units. For polymers **4a** and **4b** a similar ratio cannot be observed; nevertheless, in these cases oxygen is incorporated as well. The incorporation of oxygen into the polymer sample during thermal cross-linking in air could be demonstrated also by IR spectroscopy. The IR spectrum of the polyester **4a** cross-linked under nitrogen was subtracted from the IR spectrum of the same sample cross-linked in air. The difference spectrum showed characteristic stretching vibrations of unsaturated C=O bonds at 1698 cm^{-1} and C–O bonds at 1061, 1055, 1029, and 996 cm^{-1} often appearing as doublets and bending vibrations for C–O bonds at 1408 and 1282 cm^{-1}. Whether the susceptibility of the explosive decomposition of **2** arises from the incorporation of oxygen or from the strain that results from cross-linking cannot be decided unambiguously yet. However, it is conceivable that in the case of polycarbonate **2** the lack of a flexible spacer between the conjugated acetylene groups is the main reason for the explosive decomposition. The peroxide formed during cross-linking in air might play the role of an initiator. It can also be excluded that the carbonate functional group absorbs oxygen from the air by photooxidation, leading to an explosive decomposition. In our laboratory polycarbonates with allyloxymethylene side groups were cross-linked in air either photochemically or thermally; an explosive decomposition never could be observed.[15]

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(16) Polycarbonate 2 decomposes explosively (a) during thermal cross-linking (several times), (b) by mechanical shock of the cross-linked product, and (c) during an attempt to record a Raman spectrum at low temperature (−80 °C). Due especially to the last decomposition of the polycarbonate 2, we decided not to continue these experiments.

Registry No. 1, 128709-28-4; **2**, 63354-77-8; **3a**, 128709-29-5; **3b**, 109550-32-5; **4a**, 128709-30-8; **4b**, 63354-71-2.