Photocopolymerizations of Electron-Rich Olefins with Electron-Poor Olefins by Irradiation of Their EDA Complexes

Cherylyn Lee and H. K. Hall, Jr.*

C.S. Marvel Laboratories, Chemistry Department, University of Arizona, Tucson, Arizona 85721. *Received November 20, 1987*

ABSTRACT: Copolymerization in absence of sensitizers was induced by ultraviolet irradiation of the electron donor–acceptor complexes formed between weak donors and strong acceptors or the reverse. The most successful cases were maleic anhydride or *N*-carbethoxymaleimide with *p-tert*-butylstyrene. As solvents, less polar 1,2-dichloroethane gave better results than more polar acetonitrile. An indirect correlation was found with various measures of the donor and acceptor strengths of the respective olefins but not with their electron donor–acceptor complexes. The rather few successful copolymerizations tended to involve stronger donors with weaker acceptors and the converse rather than strong–strong or weak–weak combinations. Initiation caused by irradiation of electron donor–acceptor complexes is concluded to be a very limited technique.

Introduction

We have been engaged in a systematic study of the spontaneous thermal copolymerization of electron-rich olefins with electron-poor olefins ("charge-transfer initiation").[1] Our results have shown that such initiations proceed by way of "charge-transfer" complexes, better called electron donor–acceptor complexes, EDA. These collapse to the tetramethylene intermediates, either polar diradical or zwitterionic, which can initiate free radical copolymerization or ionic homopolymerization of the components, respectively.[2,3] In the case of weaker donors and acceptors, no spontaneous polymerizations are observed, even though EDA complexes are formed.

Absorption of ultraviolet or visible light by irradiation of an EDA complex produces an excited complex, which has been identified as the ion radical pair of the donor and acceptor by means of time-resolved laser spectroscopy.[4] In [2 + 2] cycloaddition reactions, 1,4-diradical tetramethylenes, obtained from bond formation in the contact ion radical pair, have been proposed by several authors as intermediates.[5–7]

In this paper, we inquire whether irradiation of EDA complexes of weaker donors and acceptors, which are polymerizable, can lead to 1,4-diradical tetramethylenes, which in turn can initiate radical polymerization.

Background

Surprisingly few cases of photoinduced radical copolymerizations in absence of photosensitizers have been previously reported. Only the work of Raetzsch describes irradiation of an EDA complex and the resulting copolymerization.[8,9] For the styrene–maleic anhydride system, he showed that copolymerization rates were proportional to the square root of light intensity. Maximum rates were found at high maleic anhydride concentration. As the donor ability of the solvent increased, initial polymerization rates decreased, perhaps owing to competitive complexes of maleic anhydride with solvent.

Experimental Section

General Methods. ^{1}H NMR spectra were taken on Varian EM360L and Bruker WM 250 spectrometers at 60 and 250 MHz, respectively; tetramethylsilane (TMS) was used as an internal reference. Melting points were taken on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. UV spectra were recorded on an IBM 9420 UV spectrophotometer or Perkin-Elmer Model 552 spectrophotometer. Elemental analyses were performed by Desert Analytics (formerly MicAnal), Tucson, AZ.

Purification of Solvents and Monomers. 1,2-Dichloroethane was washed with concentrated H_2SO_4, distilled water, 10% NaOH, and distilled water. It was then dried over Na_2SO_4, refluxed with CaH_2, and distilled. Acetonitrile was refluxed with CaH_2 and distilled. All solvents were stored over 4-Å molecular sieves.

All reagents were obtained from Aldrich, unless otherwise specified. *p-tert*-Butylstyrene (Polysciences), *p*-methylstyrene, *p*-methoxystyrene, methyl acrylate (Eastman Kodak), and α-methylene-γ-butyrolactone were purified by vacuum distillation from CaH_2. Maleic anhydride was vacuum distilled in a Kugelrohr apparatus. Fumaronitrile, dimethyl fumarate, and itaconic anhydride were recrystallized from benzene/petroleum ether, chloroform/petroleum ether, and diethyl ether, respectively. All monomers were stored in a desiccator at 0 °C.

Monomer Syntheses: *p*-(Isoamyloxy)styrene. *p*-Hydroxybenzaldehyde was converted to the isoamyloxy derivative by using a literature procedure for alkylation.[10] *p*-(Isoamyloxy)benzaldehyde was isolated by vacuum distillation form CaH_2 (107–111 °C (0.35 mmHg)) for a 36% yield. IR (neat): 2955, 2871, 2733 (C—H str); 1692 (C=O); 1600, 1576, 1508, 832 (phenyl); 1256, 1056 (C—O) cm^{-1}. NMR ($CDCl_3$): δ 9.87 (s, 1 H), 7.80 (d, 2 H), 6.95 (d, 2 H), 4.02 (t, 2 H), 1.70 (m, 3 H), 0.90 (d, 6 H). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 74.99; H, 8.58.

p-(Isoamyloxy)styrene was prepared by a Wittig reaction between methyltriphenylphosphonium bromide and the benzaldehyde derivative, according to a literature procedure.[11] A 50% yield of the (*p*-isoamyloxy)styrene was obtained after vacuum distillation (63–64 °C (0.02 mmHg)). IR (neat): 3086, 3064, 3038 (=C—H str); 2956, 2870 (aliph C—H str); 1626 (C=C); 1249, 1061 (C—O); 1026, 988, 898 (=C—H bend) cm^{-1}. NMR ($CDCl_3$): δ 7.30 (d, 2 H), 6.80 (d, 2 H), 6.50 (d, 1 H), 5.50 (dd, 1 H), 5.05 (dd, 1 H), 3.90 (t, 2 H), 1.65 (m, 3 H), 0.95 (d, 6 H).

***p*-(2-Chloroethoxy)styrene** was prepared in a similar fashion. 1,2-Dichloroethane was used as both the alkyl halide and solvent in the etherification of *p*-hydroxybenzaldehyde to give *p*-(2-chloroethoxy)benzaldehyde: yield 48.0%; bp 105–122 °C (0.02–0.13 mmHg). NMR ($CDCl_3$): δ 9.85 (s, 1 H), 7.80 (d, 2 H), 6.96 (d, 2 H), 4.30 (t, 2 H), 3.80 (t, 2 H) ppm.

p-(2-Chloroethoxy)styrene was prepared from the aldehyde by a Wittig reaction, was distilled in a Kugelrohr apparatus (110–120 °C (0.025 mmHg)): yield 35%. IR (KBr): 3087 (=CH str); 2919, 2869; 1625 (C=C str); 1606, 1575, 1509 (phenyl); 1433, 1409 (=CH bend); 1254, 1041 (C—O); 990, 898 (=CH bend) cm^{-1}. NMR ($CDCl_3$): δ 7.25 (d, 2 H), 6.80 (d, 2 H), 6.45 (d, 1 H), 5.50 (dd, 1 H), 5.05 (dd, 1 H), 4.20 (t, 2 H), 3.75 (t, 2 H).

***N*-(Carbethoxy)maleimide.** This compound, mp 58–59 °C (lit.[13] mp 59–61 °C; lit.[12] 58–59 °C), was prepared by the procedure described in the literature.[12,13]

Photochemical Equipment. The photochemical equipment was mounted on an optical bench to assure that the conditions were identical for all the runs. The lamp was a 100-W high-pressure short arc mercury lamp (Ultraviolet Products, Inc., type 110-1002). The light was focused with a series of glass collating lenses, followed by a narrow band interference filter (404.7 nm, Melles-Griot 03FIM002; or 365 nm, Melles-Griot 03FIM028) which was used to provide excitation with only one wavelength. The irradiated area was a circle with a 1-cm diameter; this corresponds to approximately 25% of the volume of the reaction mixture.

Photocopolymerization. The acceptor (5 mmol) was dissolved in a few milliliters of dry solvent in a 5 mL volumetric flask. After the acceptor completely dissolved, the donor (5 mmol) was added

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and the volume of the mixture adjusted by adding solvent. The solution was poured into a Pyrex irradiation vessel (18-mm diameter) and degassed three times by the standard freeze–thaw method under argon.

The reaction mixture was irradiated under a positive argon pressure with magnetic stirring. The copolymerizations were stopped if the mixture became too viscous to stir or sometimes after a minimum time of 24 h of irradiation. Irradiation of a monomer mixture without stirring produced a solid copolymer which adhered to the wall of the reaction tube in the exact area exposed to the light and grew toward the center of the tube.

Conversions were measured either gravimetrically at the end of the irradiation or by measuring the decrease in the donor monomer concentration by size exclusion chromatography during the irradiation. The donor concentration was measured by using an IBM GPC/SEC pore type A column (linear molecular weight range 100–900) and a Spectra Physics UV detector (254 nm), calibrated with standard concentration solution of the donor monomer. Some photocopolymerizations could not be followed by this method due to the high viscosity of the reaction mixture, preventing the accurate measurement of a reaction aliquot.

The copolymers were precipitated twice in ether. Elemental analysis of the polymers verified each was a 1:1 copolymer of the donor and acceptor monomers.

Ultraviolet–Visible Spectroscopy of EDA Complexes. In order to measure the absorption spectra of an EDA complex, we had to subtract the interfering monomer absorptions from the spectrum. Equal concentrations (0.2 M) of the donor and acceptor were mixed in a quartz cuvette with a 1-mm or 10-mm path length. The reference cell consists of two 4-mm path length cells in sequence, containing the unmixed monomers. Because of the difference in the path length of the sample and reference cell, the monomer absorbances were matched by making the sample monomer concentrations 80% of those of the reference solutions.

Results

Designing a system to study photoinitiation by EDA complex excitation exclusively was not trivial. Three aspects required consideration: (1) the light absorption; (2) the selection of a solvent; and (3) the selection of appropriate donor and acceptor monomers.

Light Absorption. EDA complexes with weak donor–acceptor interactions tend to absorb close to the parent monomer. Although there may be significant overlap of the EDA absorption band and the monomer absorption bands, the EDA bands generally extend out to long wavelengths. UV scans of concentrated solutions (1 M) of each monomer, showing sharp cutoffs, verified that there is no "tailing" absorption of the monomers at the wavelengths used to excite the EDA complexes.

Solvent. Dissociation of the excited complex to the solvated free ions is known to be favored in polar solvents. By carefully choosing a nonpolar solvent, we hoped to favor formation of a radical intermediate and avoid formation of the free ion radicals, putative initiators of ionic homopolymerizations. The solvent should not interfere with the donor–acceptor interaction of the monomers, although little is known about the role of the solvent in donor–acceptor systems. Cyclic ethers are known to compete with other donors for the acceptor[14-19] and were therefore excluded.

In order to favor polymerization over cycloaddition, the solvent must be suitable for preparing concentrated monomer solutions (1 M). The solubilities of the resulting copolymers must also be taken into account. 1,2-Dichloroethane and acetonitrile were suitable solvents for the copolymerizations. Although acetonitrile is fairly polar, monomer and copolymer solubilities necessitated its use.

Donor Monomers. Five para-substituted styrenes were selected as donor monomers to provide sufficiently light-absorbing EDA complexes and a range of donor strength. *p*-Methylstyrene, *p*-*tert*-butylstyrene, and *p*-methoxystyrene were commercially available, while *p*-(isoamyloxy)styrene and *p*-(2-chloroethoxy)styrene were synthesized by conventional methods.

Table I
Oxidation Potential and Valence Ionization Energy of Various Donors

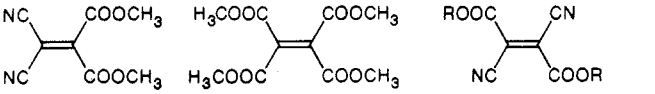
donor	E_p (V)[a]	I (eV)[b]
styrene	1.95	8.45
p-methylstyrene	1.38	8.20
p-(2-chloroethoxy)styrene		8.10
p-methoxystyrene	1.15	8.00

[a] E_p vs $Ag/AgNO_3$ (0.1 M) in CH_3CN.[20,21] [b] From photoelectron spectroscopy.

Relative donor strengths of the styrenes may be determined from their oxidation potentials. Stronger donors are more easily oxidized than weak donors. The oxidation potentials[20,21] show that the alkoxy-substituted styrenes are stronger donors than the alkyl-substituted styrenes (Table I).

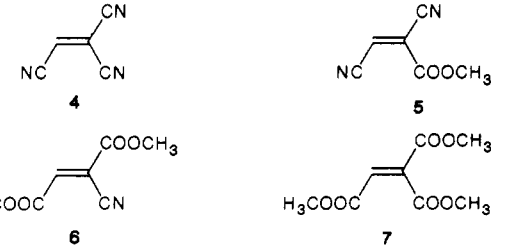
These values were confirmed by measuring the valence ionization energies (I) of the donors by ultraviolet photoelectron spectroscopy (PES) in the gas phase. PES provides the energies of the valence molecular orbitals of the donor. Strong donors will have lower ionization energies than weak donors. The HOMO of the donor styrenes is the b_1 (π) orbital of the phenyl ring.[22,23] The order of the donors by strength is *p*-methoxystyrene ~ *p*-(isoamyloxy)styrene > *p*-(2-chloroethoxy)styrene > *p*-methylstyrene ~ *p*-*tert*-butylstyrene.

Acceptor Monomers. Tetrasubstituted olefins[24,25] were first considered for this study, but they proved to be inappropriate for our intentions. Olefin **1** undergoes spontaneous thermal copolymerization with *p*-methoxystyrene, making it impossible to distinguish between the photochemistry and the thermal chemistry. Cooling the reaction mixture to 0 °C during irradiation did not eliminate or slow the thermal reactions. Olefin **2** is unreactive not only under thermal conditions but also under photoconditions. Olefin **3** presents solubility problems, even in the case of the butyl ester, due to the high degree of symmetry.



1 **2** **3**, R = CH_3 or $(CH_2)_3CH_3$

Trisubstituted acceptor olefins **4**–**7**[25] are too reactive, even at 0 °C. They spontaneously copolymerize or form small molecule products with styrene donors. Again this does not allow distinction between the photo and thermal processes. Lower temperatures create practical experimental problems, such as low solubility and excessive water condensation.



4 **5** **6** **7**

Disubstituted acceptor olefins, which are much weaker acceptors, were also considered. These have been used in other photochemical investigations, and were found to be suitable for our study. Olefins **8**–**11** are all commercially available, with the exception of **9b**, which was prepared

Table II
UV Data of EDA Complexes[a]

acceptor	parasubst of styrene (donor)	λ_{max} (nm)	A^b
dimethyl fumarate	$O(CH_2)_2CH(CH_3)_2$	324	1.69
	OCH_2CH_2Cl	329	0.838
	$C(CH_3)_3$	312	0.688
	CH_3	312	0.938
fumaronitrile	$O(CH_2)_2CH(CH_3)_2$[c]	360	2.56
	OCH_2CH_2Cl[c]	350	2.70
	$C(CH_3)_3$[d]	350	1.87
	CH_3	350	2.27
maleic anhydride	$O(CH_2)_2CH(CH_3)_2$[d]	340	0.480
	OCH_3[d]	335	0.525
	OCH_2CH_2Cl[d]	335	0.452
	$C(CH_3)_3$[c]	330	0.388
	CH_3[c]	330	0.424

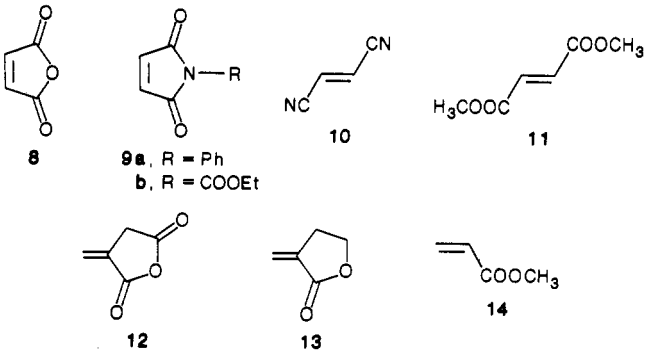
[a] All measurements made in $CHCl_3$ at room temperature (26 °C); [D], [A] = 0.2 M; maleic anhydride complexes measured in 1-mm cell; others measured in 10-mm cell. [b] Absorbance. [c] Monomer pairs that successfully undergo photoinduced copolymerization. [d] Monomer pairs that do not undergo photoinduced copolymerization.

according to the literature.[12,13] There is no problem of competing thermal chemistry with acceptors; this allowed convenient handling of the donor–acceptor mixtures during the preparation for irradiation.

Olefins **12–14** have only one electrophilic substituent and were also tested; no thermal chemistry is observed in the presence of the styrene derivatives.

The relative acceptor strengths of some acceptor olefins are known from their reduction potentials:[26] fumaronitrile **10** (E_p < −2.0 eV) < maleic anhydride **8** (E_p < −1.10 eV) < tetracyanoethylene (E_p = −0.20 eV).

EDA Complexes. Several EDA complexes were characterized by UV spectroscopy. The wavelength at maximum peak height (λ_{max}) and the absorbance (A) are listed in Table II. No equilibrium constants K could be determined because these complexes between rather weak donors and acceptors were too weak. The molar extinction



coefficients ϵ are also very low: if we assume that the k values are in the 0.1–0.2 L·mol^{-1} range,[27,28] the ϵ values are in the 100–200 L·mol^{-1}·cm^{-1} range.

By examining a series of donors with acceptors of varying strength, we hoped to correlate the absorbance region and/or intensity of an EDA complex with the ability to photoinduce copolymerization. By comparison of donor–acceptor pairs that may be photocopolymerized and the UV characterization of the EDA complexes (Table II), no such correlation is evident.

Photocopolymerizations. Several monomer combinations were irradiated at either 365 or 405 nm. In all cases, only the EDA complex was irradiated. The successful runs are listed in Table III. In these cases, a low to moderate conversion to high molecular weight copolymer was obtained.

Several monomer combinations did not yield polymer under these conditions. In Table IV, the monomers are listed according to acceptor or donor strength, and we indicated if the photopolymerization was successful or not. Stronger donors copolymerize with weaker acceptors while stronger acceptors only copolymerize with weaker donors. All the attempted combinations of monomers led to polymer once the filter was removed and the monomers were also irradiated.

Table III
Photoinduced Radical Copolymerizations[a,b]

acceptor	parasubst of styrene (donor)	solv	time (h)	wavelength (nm)	% convn	η_{inh}[g] (dL·g^{-1})
maleic anhydride	*tert*-butyl	CH_3CN	>44	365	35	0.81
maleic anhydride[c]	*tert*-butyl[c]	CH_2ClCH_2Cl	8	405	10	
N-carbethoxymaleimide	methoxy	CH_2ClCH_2Cl	25	365	15	0.76
N-carbethoxymaleimide	methoxy	CH_3CN	23	365	0	
N-carbethoxymaleimide[d]	*tert*-butyl[e]	CH_2ClCH_2Cl	44	365	26	1.49
N-carbethoxymaleimide[e]	*tert*-butyl[d]	CH_2ClCH_2Cl	16	365	16	
fumaronitrile	isoamyloxy	CH_2ClCH_2Cl	23	405	7	
fumaronitrile	isoamyloxy	CH_3CN	24	405	0	
fumaronitrile	2-chloroethoxy	CH_2ClCH_2Cl	17	405	8[f]	
itaconic anhydride	methoxy	CH_2ClCH_2Cl	10.5	405	11	
α-methylene-γ-butyrolactone	methoxy	CH_2ClCH_2Cl	>72	365	4	

[a] Additional monomer pairs at 1 M concentrations which did not copolymerize under these conditions were maleic anhydride with *p*-(isoamyloxy)- or *p*-(2-chloroethoxy)styrene in 1,2-dichloroethane (DCE), maleic anhydride with *p*-methoxystyrene in acetonitrile, fumaronitrile with *p*-*tert*-butylstyrene in (DEC), or methyl acrylate with *p*-methoxystyrene in DCE. [b] Monomers initially 1 M except as indicated. [c] 0.5 M. [d] 1.5 M. [e] 0.75 M. [f] Polymer precipitated. [g] Inherent viscosity measured at 30 °C; concentration 0.5 g·dL^{-1} in acetonitrile.

Table IV
Polymerizability of Donor–Acceptor Pairs

		acceptor, → increasing acceptor strength				
	donor (styrenes)	methyl acrylate	itaconic anhydride	fumaronitrile	*N*-carbethoxy-maleimide	maleic anhydride
↓	*p*-methyl			trace		yes
increasing	*p*-*tert*-butyl		no	no	yes	yes
donor	*p*-(2-chloroethoxy)			yes		no
strength	*p*-methoxy	no	yes		yes	no
	p-isoamyl			yes		no

Among the monoactivated olefins, itaconic anhydride was surprisingly reactive with *p*-methoxystyrene (11% conversion in 10 h). On the other hand, α-methylene-γ-butyrolactone and methyl acrylate were unreactive. The combination of the exo-methylene group, providing a less hindered site for bond formation, and the electron-poor anhydride group may make itaconic anhydride particularly reactive toward photocopolymerization.

The high molecular weight copolymers are cast easily into transparent films. The rather high molecular weight of the copolymers is attributed to a low concentration of the initiating species in the presence of a high monomer concentration.

The photopolymerization usually stops at some time during the irradiation perhaps because there is an internal filter effect. The copolymer product may compete with one of the monomer components by forming an excited complex with the other monomer. By competing for complex formation the copolymer serves as a quencher of the excited complex of the donor monomer with the acceptor monomer.

Solvent Effects. A pronounced solvent effect on copolymerization tendency is shown by the data in Table III. Fumaronitrile was copolymerized with *p*-(isoamyloxy)-styrene, and *N*-carbethoxymaleimide with *p*-methoxystyrene in 1,2-dichloroethane. No copolymerization in either case occurred when acetonitrile was used under identical conditions. For the maleic anhydride/*tert*-butylstyrene pair, the copolymerization was much slower in acetonitrile (<5% conversion in 8 h) than in dichloroethane (10% in 8 h). A comparison of solvents in irradiations of other combinations of donors and acceptors was not possible due to the limitation of the copolymer solubilities.

Discussion

This is the first systematic study that attempts the elucidation of the initiation mechanism of photoinduced radical copolymerizations by means of physical organic methods, such as examining the effects of structural variation, donor and acceptor strength, and solvent effect. However, our overall conclusion is that copolymerization initiated by photoirradiation of EDA complexes is very inefficient. As a general result, this type of initiation is far too limited and slow to be useful.

The photoinitiation depends on the relative donor and acceptor strengths of the monomers. The highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor must be at the appropriate energy levels in order to produce a radical initiating species upon photoexcitation of the electron donor–acceptor (EDA) complex. If the donor–acceptor interaction is too weak, no copolymerization occurs, as very few monomer units will be associated in an EDA complex. Also, the excited complex (contact ion radical pair) presumably decays back to the ground state faster than producing an initiating species. If the donor–acceptor interaction is too strong, the excited complex dissociates to the free ions. These can initiate ionic homopolymerization[29,30] rather than radical copolymerization. Therefore weak donor–strong acceptor monomer combinations or the reverse are appropriate for photoinduced radical copolymerization.

We were unable to study the strong EDA complexes because of competing thermal reactions. This need to exclude strong donor–acceptor pairs restricted our study in two ways. First, the selective irradiation of the EDA complex becomes more difficult because the weaker EDA complex absorptions overlap significantly with the monomer absorptions. Second, large variations in the monomer concentration, required for kinetics studies, are not possible because the monomer concentration must be high enough to ensure a sufficient EDA complex concentration.

The solvent may determine the course of the reaction. In two cases, copolymerizations that could be photoinduced in 1,2-dichloroethane could not be photoinduced in acetonitrile. Dissociation of the excited complex (contact ion radical pair) is favored in polar solvents, such as acetonitrile, which are able to stabilize the ion radicals. Although free ion radicals are known to initiate cationic homopolymerization, no homopolymer of the donor is obtained here because acetonitrile solvent does not tolerate cationic polymerization.

The slow initiation is probably due to the low quantum efficiency for the formation of the initiating species relative to other available processes; only a very small fraction of the complexes that become excited produce a radical initiating species because processes, such as back electron transfer for example, are faster.

The radical initiating species has not been identified in this study. The putative diradical tetramethylene intermediate could be formed directly from the singlet excited complex (contact ion pair), from the geminate pair of ion radicals, or from the triplet excited complex. "Bond-Forming Initiation" may yet serve as a unifying mechanism for the spontaneous thermal polymerizations and photoinduced polymerizations.

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Registry No. (Maleic anhydride)(*tert*-butyl-*p*-styrene) (copolymer), 96231-96-8; (itaconic anhydride)(methoxy-*p*-styrene) (copolymer), 60608-82-4; (*N*-carbethoxymaleimide)(methoxy-*p*-styrene) (copolymer), 116234-59-4; (*N*-carbethoxymaleimide)(*tert*-butyl-*p*-styrene) (copolymer), 116234-54-9; (fumaronitrile)(isoamyloxy-*p*-styrene) (copolymer), 116234-56-1; (fumaronitrile)((2-chloroethoxy)-*p*-styrene) (copolymer), 116234-58-3; (α-methylene-γ-butyrolactone)(methoxy-*p*-styrene) (copolymer), 116234-60-7.

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Photochemical Synthesis of Block Polymers of Poly(bisphenol A carbonate) with Vinyl Monomers

Takao Doi and Georges Smets*

Laboratory of Macromolecular and Organic Chemistry, Katholieke Universiteit Leuven, Leuven, Belgium. *Received February 25, 1988*

ABSTRACT: The photochemical synthesis of block polymers of poly(bisphenol A carbonate) (PC) and polyvinyl monomers is based on the incorporation of benzoin methyl ether (BME) in the PC main chain. On photolysis these light-sensitive PCs degrade, and the number of chain scissions per macromolecule corresponds to their NMR analytical BEM content. Upon photolysis in the presence of vinyl monomers (methyl methacrylate, ethyl acrylate, acrylonitrile), block polymers were obtained of which the composition, molecular weights, and some physical properties have been determined. The method is selective and highly efficient.

The selective incorporation of light-sensitive groups within a condensation polymer offers on photolysis the possibility of formation of macroradicals which may initiate the polymerization of vinyl monomers[1] with the production of block polymers. Depending on the mode of termination of these monomers and on the number of incorporated photolabile groups, the overall structure of the resulting block polymers will be different. If the polymer contains only one photolabile group per macromolecule, the final structure will be of the AB or/and A–B–A type, corresponding to respectively disproportionation and addition termination. If the number of light-sensitive groups exceeds unity, the block polymer mixture will also contain B–A–B triblocks and $(A–B)_n$ multiblocks, resulting from the middle labile group. These different possibilities are represented in Figure 1.

In these systems homopolymer formation will be very limited; it may result in the initiation step from a transfer reaction between the macroradical and the vinyl monomer, e.g., hydrogen transfer, or in the propagation reaction from transfer between a growing chain and the monomer. The method requires therefore an adequate choice of photolabile group and of vinyl monomer. A high quantum yield of photolysis of the photolabile groups enhances considerably the selectivity of the method. Prolonged irradiation may indeed induce undesirable side reactions, e.g., hydrogen abstraction, formation of homopolymers, or graft polymers.

A first example of this method was based on the incorporation of ketooxime ester groups in a poly(tetrachlorobisphenol A adipate). On photolysis in the presence of styrene high yields of block polymers were obtained; only 5–10% homopolystyrene was formed.[2,3] Mezger and Cantow described the incorporation of diaryl disulfide groups in a cellulosic prepolymer; on irradiation in the presence of styrene or of chloroprene these groups produce multiphase block polymers.[4] Similarly, Vlasov et al. prepared symmetric polypeptide chains containing photolabile disulfide or azo groups which on photolysis in the presence of several vinyl monomers produce polypeptide–polyvinyl block polymers.[5]

In the present paper photochemical block polymerization was based on the incorporation of *p,p'*-dihydroxybenzoin methyl ether groups (BME) in poly(bisphenol A carbonate). Its photolysis in the absence and presence of vinyl monomers as well as the formation of polycarbonate–polyvinyl block polymers will be considered successively.

Experimental Section

Chemicals. Vinyl monomers were freshly distilled under reduced nitrogen atmosphere before use. Bisphenol A was recrystallized from toluene. Tetrahydrofuran was distilled after refluxing over sodium metal for 2 h. Pyridine and acetone were dried over molecular 4A sieves. The other substances (chemical pure grade) were used without further purification.

Syntheses. *p,p'*-Dihydroxybenzoin methyl ether (BME) was prepared in a four-step synthesis: (a) methoxymethylation of *p*-hydroxybenzaldehyde, (b) benzoin condensation of the protected hydroxybenzaldehyde, (c) methylation of the secondary alcohol, and (d) deprotection of the phenol group.

(a) 4-(Methoxymethoxy)benzaldehyde was prepared by condensation of 4-hydroxybenzaldehyde in chloroform solution with dimethoxymethane in the presence of *p*-toluenesulfonic acid following the method of Yardly:[6] yield 72%; bp 97–100 °C/1 mmHg. (b) 4,4'-Dimethoxymethoxybenzoin was prepared by condensation of the preceding compound in the presence of potassium cyanide:[7] yield 42%; mp 85–87.5 °C.

Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07; O, 28.88. Found: C, 64.97; H, 6.14; O, 28.92. (c,d) 4,4'-Dimethoxymethoxybenzoin was methylated quantitatively by methyl iodide in anhydrous tetrahydrofuran in the presence of silver oxide.[8] The resulting yellow oil was hydrolyzed at 75 °C in 50% acetic acid for 10–15 min in the presence of sulfuric acid as catalyst.[7] After recrystallization from benzene, the yield was 66%, mp 189–192 °C.

4,4'-Bis((chlorocarbonyl)oxy)benzoin Methyl Ether. BME (1 g, 3.9 mmol) was dissolved in 30 mL of anhydrous tetrahydrofuran, and 6.2 g of phosgene (6.3×10^{-2} mol) was introduced. A solution of *N,N*-dimethylaniline in 30 mL of anhydrous tet-

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