Macromolecules **1989,** *22,* 4455–4462

(24) Saito, H.; Kameyama, M.; Kodama, M.; Nagata, C. *J. Biochem.* **1982,** *92,* 233.
(25) Saito, H.; Tabeta, R.; Shoji, A.; Ozaki, T.; Ando, I.; Miyata, T. *Biopolymers* **1984,** *23,* 2279.
(26) Ando, S.; Yamanobe, T.; Ando, I.; Shoji, A.; Ozaki, T.; Tabeta, R.; Saito, H. *J. Am. Chem. Soc.* **1985,** *107,* 7648.
(27) Saito, H.; Ando, I. *Annu. Rep. NMR Spectrosc.* **1989,** *21,* 210.
(28) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981,** *14,* 223.
(29) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979,** *12,* 762.
(30) Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982,** *15,* 208.
(31) Sheppard, N. J.; Szasz, G. J. *J. Chem. Phys.* **1962,** *17,* 86.

Real-Time Kinetic Study of Laser-Induced Polymerization

C. Decker* and K. Moussa

Laboratoire de Photochimie Générale (CNRS), Ecole Nationale Supérieure de Chimie de Mulhouse, 3 Rue Alfred Werner, 68200 Mulhouse, France.

Received February 2, 1989; Revised Manuscript Received April 14, 1989

ABSTRACT: The photopolymerization of mono- and multiacrylic monomers, induced by continuous laser irradiation at 363.8 nm, has been studied by using the newly developed real-time infrared (RTIR) spectroscopy. The polymerization profiles were directly recorded in the millisecond time scale, thus allowing a precise evaluation of the reaction rate, the photosensitivity, the polymerization quantum yield, the induction period, and the polymer unsaturation content. The effect of the photoinitiator, the monomer functionality, and atmospheric oxygen is substantial and was quantified. The system that performed best contains 2,2-dimethoxy-2-phenylacetophenone as photoinitiator, a polyurethane diacrylate oligomer, and a [(dimethylmethoxy)formamido]ethyl monoacrylate monomer. Polymerization was shown to develop mainly in the dark, after the short laser exposure, especially in the early stages of the reaction, where the postpolymerization effect was found to represent up to 90% of the total process. For the more reactive photoresist, the overall polymerization quantum yield was measured to be 3000 mol photon^{-1} in the presence of air and 13 000 mol photon^{-1} for N_2-saturated systems, corresponding to a photosensitivity of 0.7 and 0.17 mJ cm^{-2}, respectively.

Introduction

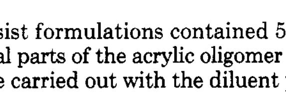
Much effort has been devoted to photopolymers over the past few years because of the distinct advantages of UV radiation initiation, mainly, the rapidity of the reaction, which lasts a fraction of a second, and the selectivity, which permits high-resolution imaging. In the continuing search for ever faster polymerizing systems, lasers have appeared recently as one of the most powerful tools to transform rapidly a liquid monomer into a solid polymer.[1-9] Pulsed lasers, which deliver a large amount of energy within a few nanoseconds, have been often employed in polymer science, in particular to obtain kinetic rate constants for free-radical polymerizations[10-14] and to evaluate the effects of the pulse frequency on the molecular weight distribution.[15-18] Continuous output lasers still present the unique advantage of providing extremely high rates of initiation that remain essentially constant throughout the polymerization. Owing to the spatial coherence of the laser beam, complex polymer patterns can be directly written onto photosensitive plates at micronic resolution.[5]

One of the critical unsolved problems in laser-initiated polymerization is finding an adequate method to study in real time the kinetics of polymerizations which develop in the millisecond range. None of the usual analytical techniques has been able to meet this challenge so far. Conventional infrared spectroscopy has proved to be valuable for evaluating the polymerization extent after a short laser exposure,[4,5] but it is based on discrete measurements and includes in the final result the postpolymerization which develops just after the UV exposure. Differential scanning calorimetry is commonly used to monitor in real time the kinetics of light-induced polymerization,[6-8] but it was found inadequate in the present case due to its response time of a few seconds. The same holds true for other techniques such as dilatometry,[19,20] IR radiometry,[21] photoacoustic spectroscopy,[22] and nephelometry.[23,24] Laser interferometry,[25] a novel method based on refractive index changes upon polymerization, was shown to be well-suited for recording polymerization profiles in the millisecond time scale, but it provides no quantitative data about the rate of the reaction and the actual degree of polymerization.

Recently, a new analytical method, based on IR spectroscopy, has been developed in our laboratory in order to follow quantitatively and in real time photopolymerizations that take place in a fraction of a second.[26] In this paper, we describe how this technique was used to study the kinetics of polymerizations initiated by continuous-wave laser beams and thus evaluate polymerization rates and quantum efficiencies for various photoresists commonly used in UV-curable coatings and adhesives. It also reports the remarkable performance of a novel acrylic monomer that contains a carbamate function in its formula and has the unique advantage of polymerizing both rapidly and extensively.

Experimental Section

Materials. The photopolymerizable resins used in this work contained three main components: (i) a photoinitiator that cleaves readily upon laser exposure to generate free radicals (for most experiments, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651 from Ciba Geigy) was selected because of its high initiation efficiency; (ii) an acrylate end-capped oligomer consisting of an aliphatic polyurethane (Actilane 20 from SNPE) or of a derivative from the glycidyl ether of bisphenol A (Actilane 72 from SNPE); (iii) a reactive acrylic diluent, such as hexanediol diacrylate (HDDA from UCB), trimethylolpropane triacrylate (TMPTA from UCB), ethyl diethylene glycol acrylate (EDGA from SNPE), or [(dimethylmethoxy)formamido]ethyl monoacrylate (Acticryl CL 960 from SNPE), with the following formula:



$$CH_2{=}CH\underset{\underset{O}{\|}}{C}OCH_2CH_2NH\underset{\underset{O}{\|}}{C}O\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}H$$

Typical photoresist formulations contained 5% of initiator (0.2 mol L^{-1}) and equal parts of the acrylic oligomer and diluent. Some experiments were carried out with the diluent plus photoinitiator only, in order to test the intrinsic reactivity of these various

0024-9297/89/2222-4455$01.50/0

monomers. The resin was applied as a uniform layer of controlled thickness, between 6 and 30 μm, on a NaCl disk with a calibrated wire-wound applicator.

Laser Irradiation. Samples were exposed to the radiation of a continuous-wave argon ion laser (Spectra Physics, Model 2000) turned to its UV emission line at 363.8 nm. The radiant power (P) at the sample position was measured to be in the range 30–200 mW cm^{-2}, depending on the selected laser output and on the cross section of the laser beam (0.1–1 cm^2). It corresponds to a fluence rate (I_0) between 0.9 and 6 × 10^{-7} einstein s^{-1} cm^{-2}. The irradiation was carried out at room temperature either in the presence of air or in a nitrogen-saturated reactor equipped with polyethylene windows, which are transparent to both the laser beam and the infrared analyzing beam. In order to prevent atmospheric O_2 from diffusing into the sample during the laser irradiation in the presence of air, some experiments, were carried out with laminates, the resin-coated NaCl disk being covered with a polyethylene film. The fraction (f) of the incident laser radiation absorbed by the sample was determined either by differential actinometry or from the absorbance (A) of the coating at the wavelength of the relevant laser emission.

The method used to study in real time the kinetics of ultrafast photopolymerizations has already been described.[26] The NaCl disk coated with the resin was placed in a IR spectrophotometer and exposed to the infrared and laser beams. The decrease in the IR absorbance at 810 cm^{-1} was monitored in real time on the spectrophotometer recorder operated at maximum speed (5 cm s^{-1}). The full-scale response of the recorder was measured to be 0.15 s, thus allowing a correct kinetic analysis of reactions having 50% conversion time above 0.3 s. Faster polymerizations were followed by using a transient memory recorder; the limiting factor is then the response of the IR detector, usually 30 ms.

Real-Time Infrared (RTIR) Spectroscopy

The basic principle of this new method of kinetic analysis consists in exposing the sample simultaneously to the UV laser beam, which induces the polymerization, and to the analyzing IR beam, which monitors the resulting drop in the absorbance of the reactive double bond. The IR spectrophotometer must be set in the absorbance mode and the detection wavelength fixed at a value where the monomer double bond exhibits a discrete and intense absorption, e.g., at 810 cm^{-1} for acrylic monomers ($CH{=}CH_2$ twisting). Upon laser irradiation, the fast decrease of the 810-cm^{-1} peak will accurately reflect the extent of the polymerization process since the absorbance increment $(A_{810})_0 - (A_{810})_t$ is directly proportional to the number of acrylate functions which have polymerized. Following continuously the variation of the IR signal intensity upon laser irradiation allows conversion versus time curves to be directly recorded for polymerizations developing on a time scale of less than 1 s.

Figure 1 shows a typical polymerization profile recorded by RTIR spectroscopy for an acrylic monomer (Acticryl CL 960) exposed to the 363.8-nm emission line of an argon ion laser in the presence of air. It directly translates into the dependence of the percent conversion on laser irradiation time. To the best of our knowledge, these are the first actual kinetics recorded in real time for photopolymerizations developing in such a short time scale and which transform a liquid monomer into a polymer material.

The sigmoid character of the kinetic curve can be attributed to two major factors: (i) the slight induction period observed initially is due to the well-known inhibition effect of O_2 on radical-induced polymerization,[27] (ii) the slowing down of the reaction for conversion degrees above 30% results from both the progressive depletion of the acrylic double bonds and the gel effect, with its segmental mobility restrictions.[28,29]

One of the distinct advantages of RTIR spectroscopy is that the most important kinetic parameters of a photopolymerization can be evaluated in a single experiment: the rate of the reaction, the quantum yield of polymerization, the induction period, the photosensitivity, and the residual unsaturation content of the polymer formed.

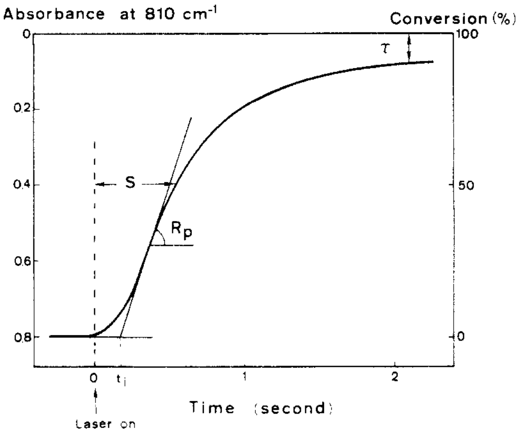


Figure 1. Photopolymerization profile recorded by RTIR spectroscopy for a monoacrylate (CL 960) exposed to the 363.8-nm emission of an Ar$^+$ laser in the presence of a photoinitiator (5% of Irgacure 651): radiant power, 100 mW cm^{-2}; film thickness, 25 μm.

The rate of polymerization (R_p) can be determined at any moment of the reaction from the slope of the RTIR kinetic curve:

$$R_p = [M]_0 \frac{(A_{810})_{t_1} - (A_{810})_{t_2}}{(A_{810})_{t_0}(t_2 - t_1)}$$

where $[M]_0$ is the monomer concentration before laser exposure. For photopolymerizations carried out in the presence of air, R_p usually reaches its maximum value at about 25% conversion,[26] since at this point O_2 inhibition has been overcome and gelification has not yet slowed down the polymerization rate.

The quantum yield of polymerization (Φ_p) reflects the efficiency of this photochemical reaction and corresponds to the number of polymerized functions per photon absorbed. It is calculated from R_p values and from the fluence rate of the laser beam (I_0):

$$\Phi_p = \frac{R_p(\text{mol L}^{-1}\ \text{s}^{-1})\ l(\text{cm})}{10^3(1 - e^{-2.3A})I_0\ (\text{einstein cm}^{-2}\ \text{s}^{-1})}$$

where A is the absorbance at 363.8 nm of the sample and l the film thickness. From Φ_p values, the kinetic chain length (Λ) of the polymerization can then be evaluated, once the initiation quantum yield (Φ_i) is known since $\Lambda = \Phi_p/\Phi_i$. In the photopolymerization of multifunctional monomers (UV-curing), where it is difficult to evaluate the molecular weight of the cross-linked polymer formed, quantum yield measurements appear to be the best method for evaluating the kinetic chain length of the reaction.

The induction period (t_i), which is observed only for experiments carried out in the presence of air, shows how effectively O_2 interferes with the polymerization process. While negligible in photocationic polymerization, this inhibition effect was found to be of great importance in radical-induced photopolymerizations,[30] which are most often carried out in thin films because of the limited penetration of UV radiation in organic materials. The use of powerful lasers, by reducing drastically the exposure time, was shown to be one of the most efficient methods for lowering air diffusion in the film and thus avoiding the deleterious effects of O_2 on the physical properties of air-cured polymers.[31]

The photosensitivity (S) of a UV-curable resin is usually defined as the amount of energy which is required

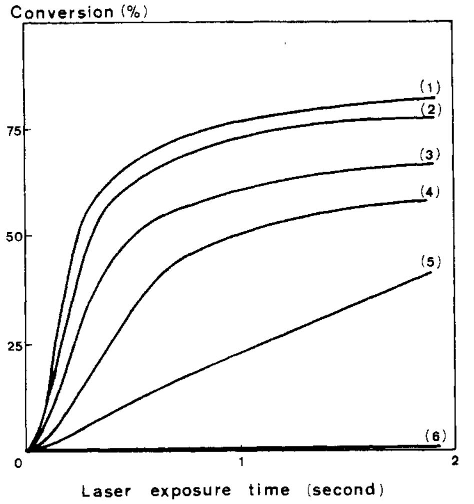


Figure 2. Influence of the photoinitiator (5%) on the laser-induced polymerization of a polyurethane diacrylate + hexanediol diacrylate resin: (1) Irgacure 907; (2) Irgacure 651; (3) Irgacure 184; (4) Darocure 1173; (5) benzophenone + N-methyl-2,2′-iminodiethanol; (6) Quantacure PDO. Radiant power = 150 mW cm^{-2}.

to polymerize half of the reactive functions. This parameter is most valuable for practical applications since it includes both the rate of polymerization and the induction period. It is expressed in mJ cm^{-2} and is determined easily from the RTIR curves by measuring the 50% conversion time ($t_{0.5}$):

$$S = t_{0.5}Pf$$

where P is the radiant power incident on the sample, expressed in mW cm^{-2}, and f the fraction of light absorbed by the sample. The lower the S value, the more sensitive the UV-curable system will be.

The residual unsaturation content (τ) of photopolymers can be quite important, especially for multifunctional monomer systems where polymerization stops at an early stage as a consequence of the network formation and the resulting drop in the segmental mobility of the growing polymer chains. One of the distinct advantages of IR spectroscopy is to afford a precise evaluation of the amount of reactive functions which remain in the final polymer and may affect its long-term stability:

$$\tau = [(A_{810})_t/(A_{810})_0][\mathrm{M}]_0$$

Its value was found to highly depend on both the monomer functionality and the chemical structure of the functionalized oligomer chain.[30]

Kinetics of Laser-Induced Polymerization

Influence of Photoinitiator. The choice of the photoinitiator is essential in laser-induced polymerization since even the most reactive acrylic monomers were found to hardly polymerize when exposed in pure form to the laser beam (less than 3% conversion after 1 min). Photoinitiators must absorbed the incident light in order to generate the electronically excited states which lead to the production of the reactive species. This requirement is crucial when lasers are used as a radiation source, owing to the monochromatic character of the emission, as illustrated by Figure 2. This figure shows the recorded RTIR polymerization profiles for a polyurethane acrylate resin containing various commercial photoinitiators upon exposure to the 363.8-nm radiation of an argon ion laser. The large differences observed in the polymerization rate can be partly accounted for on the basis of the variation in the absorbance at 363.8 nm.

Table I
Laser-Initiated Photopolymerization of a Polyurethane Acrylate with Various Commercial Photoinitiators[a]

photoinitiator	f^b	t_i,[c] s	R_p,[d] mol L^{-1} s^{-1}	S,[e] mJ cm^{-2}
Irgacure 907	0.21	0.04	11	14
Irgacure 651	0.14	0.04	10	9
Irgacure 184	0.05	0.06	5	11
Darocure 1173	0.04	0.08	3	16
benzophenone + amine	0.14	0.1	1	60
Quantacure PDO	0.05		<0.05	

[a] Radiant power of the laser emission at 363.8 nm: 150 mW cm^{-2}; [photoinitiator] = 5%; [HDDA] = 47.5% (w/w). [b] Fraction of the incident laser radiation absorbed by a 20-μm coating. [c] Induction period. [d] Maximum rate of polymerization. [e] Photosensitivity: energy required to reach 50% conversion.

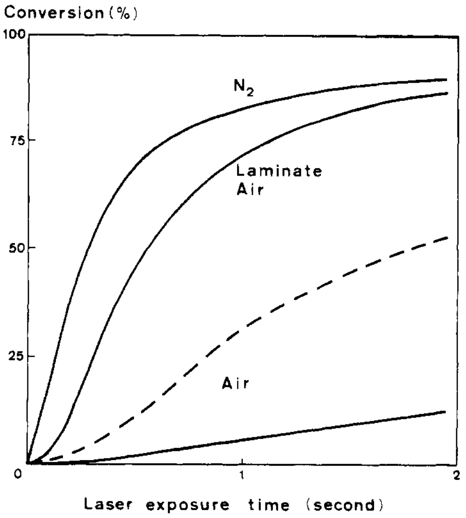


Figure 3. Influence of atmospheric oxygen on the laser-induced polymerization of a [(dimethylmethoxy)formamido]ethyl monoacrylate monomer (Acticryl CL 960): photoinitiator, Irgacure 651 (5%); radiant power, 70 mW cm^{-2}; film thickness, 5 μm (—) and 12 μm (- - -).

Table I reports the values of the fraction of laser light absorbed by a 20-μm-thick film for the different photoresists, together with the values of the maximum polymerization rate (R_p), the induction period, and the photosensitivity. The best results were obtained with DMPA, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651), which combines high sensitivity and a rapid polymerization rate. It was therefore selected as the photoinitiator in all further experiments. One may have noticed the poor performance of Quantacure PDO, an efficient photoinitiator for the curing with conventional UV radiation,[26] that proved here unable to initiate any polymerization, although it absorbs the laser emission at 363.8 nm. This suggests that the excited states formed under those conditions (nπ^* transition) are mainly disappearing by different routes which do not generate radicals capable of initiating a polymerization.

Photopolymerization of Acrylic Monomers. In the presence of DMPA, acrylic monomers were shown to polymerize readily under UV laser exposure.[3-5] With the newly developed [(dimethylmethoxy)formamido]ethyl acrylate monomer[32] (Acticryl CL 960), 50% conversion was reached within 0.25 s of exposure in an inert atmosphere (Figure 3). In thin films, the reaction is strongly inhibited by atmospheric oxygen, which diffuses into the film and interferes with the polymerization by scavenging both the initiating and the polymer radicals. This detrimental effect can be prevented to a large extent by covering the monomer coating with a polyethylene film, which is transparent

Table II
Kinetic Results of Photopolymerization of Acrylic Monomers Exposed to the 363.8-nm Emission Line of an Argon Ion Laser[a]

monomer	[acrylate]$_0$, mol L^{-1}	induction period, s	R_p(max),[b] mol L^{-1} s^{-1}	S,[c] mJ cm^{-2}	τ,[d] %
monoacrylate (EDGA)[e]	4.9	0.2	1.2	24	15
diacrylate (HDDA)[e]	8.0	0.1	4.5	12	30
triacrylate (TMPTA)[e]	9.0	0.05	8.2		60
monoacrylate (CL 960)[f]	4.5	0.05	5.0	5.7	8
polyurethane diacrylate[g] + EDGA	3.1	0.12	2.6	9	12
polyurethane diacrylate + HDDA	4.7	0.06	5.8	9	30
polyurethane diacrylate + TMPTA	5.2	0.03	10		55
polyurethane diacrylate + CL 960	2.9	0.04	11	2.5	10
polyphenoxy diacrylate[h] + EDGA	4.1	0.08	6	4	20
polyphenoxy diacrylate + HDDA	5.9	0.06	10	6	40
polyphenoxy diacrylate + TMPTA	6.3	0.04	14		60
polyphenoxy diacrylate + CL 960	4.0	0.05	15	2	15

[a] In the presence of air. Fluence rate = 2.1×10^{-7} einstein s^{-1} cm^{-2}; [Irgacure 651] = 5%; film thickness 20 μm. [b] Maximum rate of polymerization. [c] Photosensitivity = energy needed for 50% conversion. [d] Residual unsaturation in the cured polymer after 10 s of laser irradiation. [e] Polyethylene/resin/NaCl/laminate. [f] Polyethylene/resin/NaCl/laminate. [(Dimethylmethoxy)formamido]ethyl acrylate. [g] Actilane 20 50%. [h] Actilane 72 50%.

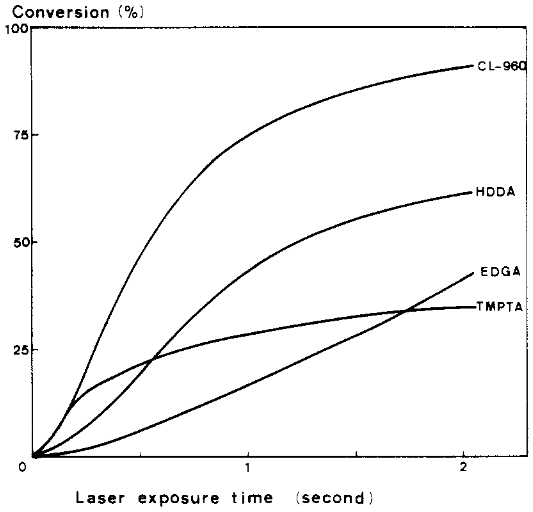


Figure 4. Photopolymerization profiles recorded by RTIR spectroscopy for various acrylic monomers exposed to the 363.8-nm laser emission, as polyethylene/resin/NaCl laminates, in the presence of air: photoinitiator, Irgacure 651 (5%); fluence rate, 2.1×10^{-7} einstein s^{-1} cm^{-2}.

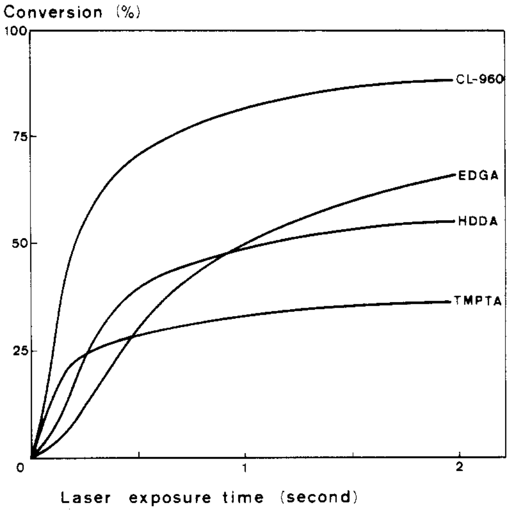


Figure 5. Influence of the diluting monomer on the polymerization of a polyurethane diacrylate photoresist exposed to the 363.8-nm laser beam in the presence of air: photoinitiator, Irgacure 651 (5%); fluence rate, 2.1×10^{-7} einstein s^{-1} cm^{-2}.

to the laser beam as well as to the IR analyzing beam. After a short induction period of about 100 ms, the polymerization develops almost as fast as in an N$_2$-saturated atmosphere (Figure 3). With such laminates, the polymerization rate was essentially unaffected by changes in the thickness of the monomer layer, whereas it was found[26] to drop sharply with the decreasing thickness of monomer films irradiated in contact with air (Figure 3).

The monomer functionality has a marked effect on the rate of polymerization and the maximum conversion, as shown by Figure 4. The following opposite trends were observed for the various acrylic monomers examined (Table II):

$$\text{reactivity:} \quad \text{mono} < \text{di} < \text{tri}$$

$$\text{maximum conversion:} \quad \text{tri} < \text{di} < \text{mono}$$

These results can be accounted for in consideration of both the higher initial concentration in acrylic groups as the functionality increases and the gelification, which limits the extent of the polymerization process. It should be stressed that the monomer Acticryl CL 960 which contains only one acrylate function exhibits a unique behavior upon laser irradiation; it polymerizes more rapidly as a diacrylate and as extensively as a monoacrylate (Figure 4 and Table II). R_p values are 4 times larger than for typical monoacrylates and as much as 40 times when compared to methacrylates. Further investigations on the photopolymerization of this new monomer and related compounds are in progress in order to elucidate the reason for this unexpectedly high reactivity.

Photopolymerization of Acrylic Resins. When a difunctional oligomer is introduced in the formulation, either a polyurethane diacrylate or a polyphenoxy diacrylate, essentially the same trend is observed, but the initial polymerization rate is markedly increased, with the expected less pronounced effect of the monomer functionality (Figure 5). This was shown to result mainly from the much higher viscosity of the resin, which favors chain propagation over termination[33] and also reduces O$_2$ diffusion into the film. The polymerization then develops effectively, even in thin films in contact with air, thus eliminating the need of laminates.

From a comparison of the results obtained with the various photoresists exposed to the 363.8-nm laser radiation (Table II), the following can be concluded. The induction period ranges between 40 and 200 ms and decreases as the monomer functionality and thus its reactivity is increased. The maximum rate of polymerization reaches values as large as 15 mol L^{-1} s^{-1}, which would correspond to a full conversion time of 0.2 s. If required, much higher R_p values can be obtained by simplifying

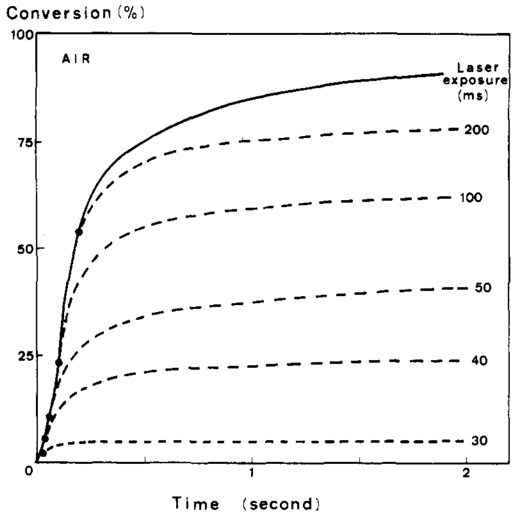


Figure 6. Kinetics of the postpolymerization in the dark, after laser exposure for various durations, of a polyurethane diacrylate + Acticryl CL 960 photoresist in the presence of air: (—) continuous irradiation; (- - -) postpolymerization effect after indicated laser exposure.

increasing the power output of the laser or by focusing the laser beam.[34] The most photosensitive systems are those containing the carbamate–acrylate monomer, where the S value drops down to 2 mJ cm^{-2}. The lowest amount of residual unsaturation was found in polymers based on monofunctional monomers and polyurethane oligomers, which exhibit the largest segmental mobility (T_g below ambient) and thus reach the highest degrees of conversion.

With respect to the considered kinetic parameters, the best performance was obtained with the following system: DMPA = 5%, Actilane 20 = 47.5%, and Acticryl CL 960 = 47.5% (weight/weight). This combines high reactivity and great sensitivity with low residual unsaturation. This photoresist was used in all the experiments described below.

Postpolymerization Study

Air-Saturated Monomers. RTIR spectroscopy proved to be a well-suited technique to study in real time the postpolymerization, which takes place in the dark after the laser has been switched off. Figure 6 shows the polymerization profiles recorded for a polyurethane acrylate photoresist exposed to the 363.8-nm laser beam for various durations, between 30 and 200 ms, in the presence of air. For exposure times shorter than 30 ms, polymerization did not occur because of the O_2 inhibition effect. At longer exposures, the monomer continued to polymerize for about 1 s after the laser irradiation. This postpolymerization effect is more important in the early stages of the reaction, where it accounts for up to three quarters of the polymer formed.

N_2-Saturated Monomers. Essentially the same trend was observed for laser-induced polymerizations carried out in a N_2-saturated atmosphere, but for shorter exposure times (Figure 7). For instance, a 3-ms laser pulse proved sufficient to polymerize more than 20% of the acrylic double bonds and over 60% for a 20-ms pulse. The postpolymerization was found to be slightly more pronounced and to last longer than in the presence of air, but it was essentially completed about 2 s after the laser had been switched off. For short exposures (<10 ms), as much as 90% of the polymerization actually takes place in the dark.

The relative importance of the postpolymerization effect decreased steadily with increasing degree of conversion, measured just at the end of the laser pulse, as shown by Figure 8. Interestingly, very similar curves were obtained in air and in nitrogen-saturated systems, which suggests that O_2 scavenging of the polymer radicals is not the predominant termination reaction. Thus, under our experimental conditions, i.e., a 20-μm-thick film of viscous resin in contact with air, the polymer chains stop growing mainly because of the usual bimolecular interactions of radicals and the trapping of radicals in the polymer matrix.[35,36] As the film thickness decreases, O_2 scavenging gains in importance and ultimately becomes the prevailing termination route.

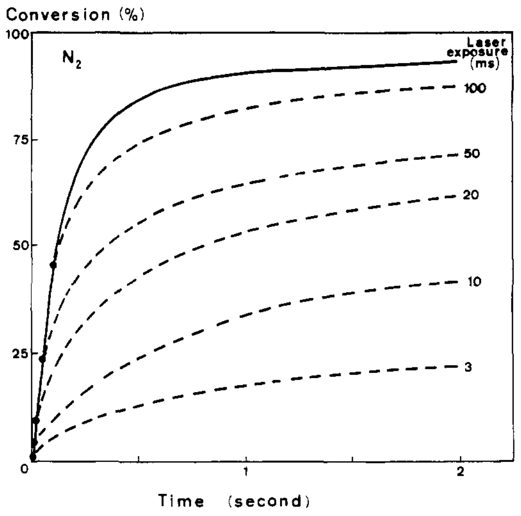


Figure 7. Kinetics of the postpolymerization in the dark, after laser exposure for various durations, of a polyurethane diacrylate + Acticryl CL 960 photoresist in pure nitrogen: (—) continuous irradiation; (- - -) postpolymerization effect after indicated laser exposure.

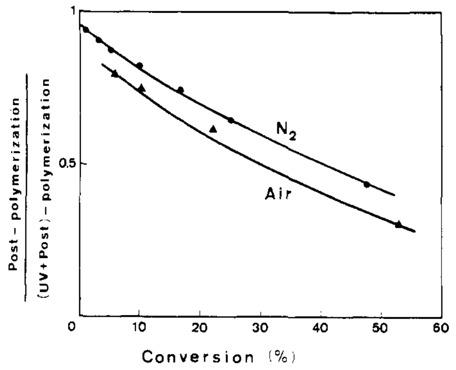


Figure 8. Relative importance of the postpolymerization as a function of the degree of conversion for a polyurethane acrylate photoresist exposed to a UV laser beam in the presence of air (▲) or pure N_2 (●).

Quantum Yield of Polymerization. The kinetic profiles of the total UV + dark polymerization were calculated from the recorded RTIR curves (Figures 6 and 7) and are represented in Figure 9 by dashed lines. From the slope of these curves and the laser fluence rate, one can evaluate the overall quantum yield of the polymerization, Φ_p. After a short induction period due to O_2 inhibition, Φ_p reaches rapidly a maximum value of 3000 mol/photon for degrees of conversion above 10%. In a pure N_2 atmosphere, the polymerization starts immediately with the laser exposure, each photon absorbed by the monomer film inducing the polymerization of 13 000 acrylic double bonds. Taking into account a quantum yield value of 0.1 for the production of initiating radicals in the photolysis of DMPA,[37] the kinetic chain length of the polymerization

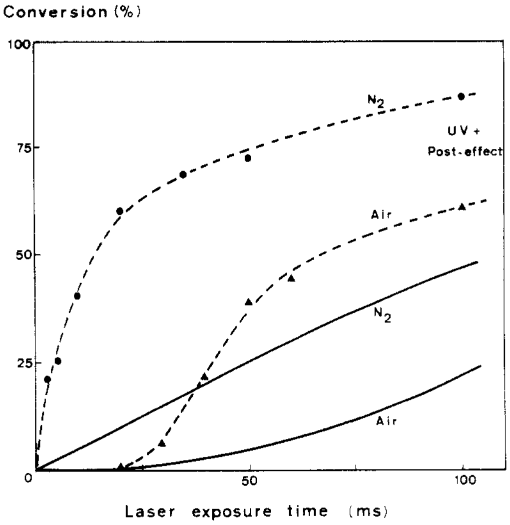


Figure 9. Kinetics of the polymerization of a polyurethane acrylate photoresist exposed to a UV laser beam in the presence of air (▲) or pure N_2 (●): (—) recorded RTIR profiles; (- - -) UV laser irradiation + 2-s postpolymerization effect.

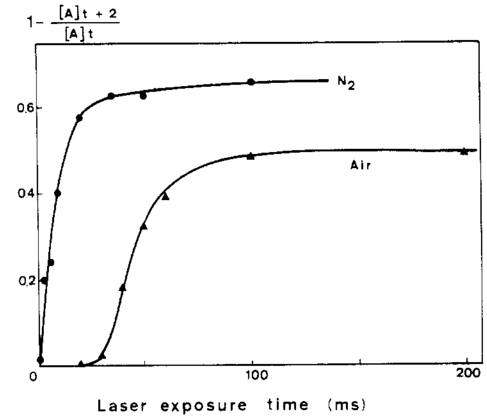


Figure 10. Growth of the radical concentration upon laser irradiation of a polyurethane acrylate photoresist in the presence of air (▲) or pure N_2 (●).

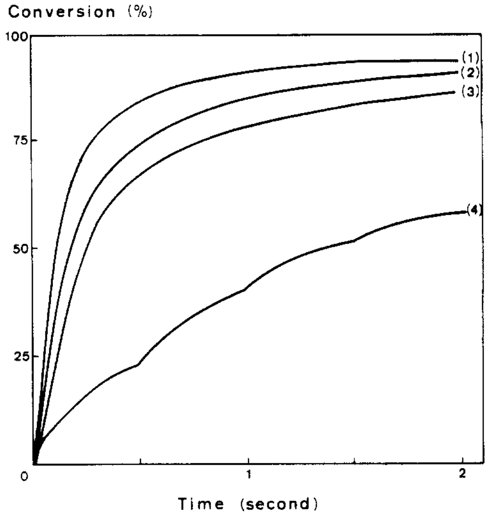


Figure 11. Photopolymerization profiles recorded by RTIR spectroscopy for a polyurethane acrylate photoresist exposed to the 363.8-nm laser emission in a pure N_2 atmosphere: (1) continuous irradiation; (2–4) intermittent irradiation with 10-ms laser pulse. Time interval between pulses: (2) 10 ms; (3) 50 ms; (4) 500 ms.

was calculated to be 130 000 acrylates polymerized per initiating radical. This rather large value shows how effectively the propagation chain reaction develops in these multifunctional monomers, despite the high rate of initiation provided by the laser irradiation (1.3×10^{-3} radical L^{-1} s^{-1}).

An interesting consequence of the substantial postpolymerization effect exemplified by this study is that the photosensitivity values, deduced from the RTIR kinetic curves and reported in Table II, must be reevaluated. According to the polymerization profiles of Figure 9, 50% conversion was reached within 15 ms in O_2-free systems and 65 ms in the presence of air, which corresponds to a photosensitivity of 0.17 and 0.7 mJ cm^{-2} respectively, i.e., a threefold improvement over the S values determined previously (Table II).

Growth of the Radical Concentration. The rate of the dark polymerization (R'_p) obeys the following equation: $R'_p = k_p[A]_t[R^\bullet]$, where $[A]_t$ is the concentration of acrylic double bonds which have not polymerized after irradiation time t and $[R^\bullet]$ the concentration of radicals (initiating + polymer) at time t. The propagation rate constant k_p was recently shown[29] to remain essentially constant in the light-induced polymerization of bulk MMA, for degrees of conversion up to 40%. If the same holds true in the present case, the extent of the postpolymerization will reflect primarily the amount of radicals which were present at the end of the laser exposure. It was calculated from the difference $[A]_t - [A]_{t+2}$, where $[A]_{t+2}$ is the acrylate concentration at time $t + 2$, since the postpolymerization effect was shown to be essentially completed 2 s after the laser exposure. This difference was then divided by $[A]_t$ to take into account the decreasing concentration of the remaining acrylic double bonds upon irradiation. The quantity $1 - [A]_{t+2}/[A]_t$, which is directly related to the radical concentration at time t, was finally plotted as a function of the duration of the laser exposure (Figure 10).

In the absence of oxygen, this ratio appears to grow rapidly as soon as the monomer film is exposed to the laser beam. It levels off to a constant value after about 30 ms, the time, t_s, needed for the radicals to reach the steady-state concentration where the rate of termination equals the rate of initiation. The amount of initiating radicals formed during that time was calculated to be 4×10^{-5} radicals L^{-1}, taking a Φ_i value of 0.1. While t_s was found to vary inversely with the fluence rate, this amount remained essentially constant. In the presence of oxygen, a similar behavior was observed, except for a 30-ms induction period, a slower radical growth, and a lower steady-state value reached after 100 ms.

Intermittent Laser Irradiation. In a recent study of the laser-pulsed photopolymerization of methyl methacrylate, Hoyle and co-workers[17,18] showed the marked effect of the repetition rate on the reaction efficiency. Shortening the time interval between successive pulses was found to decrease both the amount and the molecular weight of the polymer formed. This was explained on the basis of a premature termination of the living polymer by the radicals produced by the next pulses. In view of these results, we exposed the multiacrylic monomer films to intermittent laser irradiation, using an electronic shutter to generate 10-ms-wide pulses.

Figure 11 shows the RTIR polymerization profiles recorded when operating at a pulse interval of 10, 50, and 500 ms, with comparison to the continuous irradiation. Under those conditions, the various samples did not receive the same amount of radiation; for instance, 2 s after the laser was fired, the three samples have been exposed to 4, 33, and 100 laser shots, which corresponds to an absorbed energy of 0.4, 3.3, and 10 mJ cm^{-2}, respectively, as

Table III
Comparison of the Pulsed and Continuous Laser-Induced Polymerization of a Polyurethane Acrylate in Pure N_2[a]

		laser irradiation mode					
		pulsed			continuous		
total time, ms	energy absorbed, mJ cm^{-2}	pulse interval, ms	laser shots	conversion, %	exposure time, ms	post effect duration, ms	conversion, %
100	0.5	10	5	32	50	50	30
200	1.0	10	10	55	100	100	58
120	0.2	50	2	25	20	100	24
300	0.5	50	5	54	50	250	50
600	1.0	50	10	71	100	500	75
1020	0.2	500	2	42	20	1000	48
2040	0.4	500	4	58	40	2000	64

[a] Pulse duration = 10 ms; fluence rate = 2.1×10^{-7} einstein s^{-1} cm^{-2}.

compared to 20 mJ cm^{-2} for the continous irradiation. Whatever the repetition rate, the monomer was shown to polymerize with essentially the same efficiency as upon continuous laser irradiation, provided that the comparison is based on the total energy received and on post-polymerization effects of equal length (Table III). The lack of any significant influence of the laser repetition rate suggests that the initiator radicals produced by subsequent pulses are not playing an important role in the termination process.

The difference between the results of Hoyle et al.[17] and our results may arise from the much shorter and more intense laser pulses used by these authors that will generate higher concentrations of terminator radicals and thus favor premature bimolecular termination over propagation. In addition, chain termination by radical trapping is less likely to occur in the polymerization of a monofunctional monomer like MMA than in the cross-linking polymerization of multiacrylates.

Conclusion

RTIR spectroscopy has proved to be a most valuable technique to follow in real time and quantitatively the kinetics of laser-induced polymerizations, which develop extensively in a fraction of a second. From the conversion versus time curves that are directly recorded, the important kinetic parameters were determined for the highly reactive acrylic resins commonly used in coatings and adhesives applications. As the monomer functionality was increased, the polymerization was shown to develop faster but to stop earlier owing to gelification, thus leading to a cross-linked polymer that contains a substantial amount of unreacted acrylic double bonds. In this respect, a novel monoacrylate monomer appears to be very promising in that it combines a high degree of conversion and a great reactivity, with each photon absorbed inducing the polymerization of up to 13 000 acrylic double bonds for air-free photoresists.

After the laser exposure, the polymerization continues to proceed in the dark for about 2 s, both in N_2-saturated systems and in the presence of air. This post-polymerization effect is most important at the beginning of the photopolymerization, where it accounts for up to 90% of the total polymer formed. By studying in real time the kinetics of the postpolymerization, one can follow the early growth of the radical concentration which, under the experimental conditions, was found to level off after 30 ms of laser exposure in a N_2 atmosphere and after 100 ms in the presence of air.

The results reported in this paper show the great potential of real-time infrared spectroscopy to provide much detailed information about the polymerization kinetics of mono- or multifunctional monomers exposed to laser beams. This analytical method can be applied to other types of radiation and to any fast polymerizing system, provided it exhibits a distinct IR absorption specific of the reactive functional group.

Registry No. HDDA, 13048-33-4; EDGA, 7328-17-8; TMPTA, 15625-89-5; $CH_2{=}CHC(O)_2CH_2CH_2NHC(O)_2CH(CH_3)_2$, 116325-79-2; Irgacure 651, 24650-42-8; Actilane 20, 86003-21-6; Actilane 72, 122519-31-7; Irgacure 907, 71868-10-5; Irgacure 184, 947-19-3; Darocur 1173, 7473-98-5; benzophenone, 119-61-9; Quantacure PDO, 65894-76-0.

References and Notes

(1) Majury, T. G.; Melville, H. W. *Proc. R. Soc. London* **1959**, *205A*, 496.
(2) Sadhir, R. K.; Smith, J. D. B.; Castle, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1315.
(3) Decker, C. *Polym. Photochem.* **1983**, *3*, 131.
(4) Decker, C. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2451.
(5) Decker, C. *J. Coat. Techn.* **1984**, *56*, 29.
(6) Hoyle, C. E.; Hensel, R. D.; Grubb, M. B. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1865.
(7) Hoyle, C. E.; Hensel, R. D.; Grubb, M. B. *J. Radiat. Curing* **1984**, *11*(4), 22.
(8) Hoyle, C. E.; Hensel, R. D.; Grubb, M. B. *Polym. Photochem.* **1984**, *4*, 69.
(9) Decker, C. Proceedings of Intern. Conf. in Organic Coatings; Athens, 1988; Vol. 14, p 101.
(10) Olaj, O.; Bitai, I.; Gleixner, G. *Makromol. Chem.* **1985**, *186*, 2569.
(11) Olaj, O.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.
(12) Olaj, O.; Bitai, I. *Die Angew. Makromol. Chem.* **1987**, *155*, 177.
(13) Olaj, O.; Bitai, I. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 275.
(14) Buback, M.; Schween, J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 699.
(15) Hoyle, C. E.; Trapp, M. A.; Chang, C. H. *Polym. Mater. Sci. Eng.* **1987**, *57*, 579.
(16) Hoyle, C. E.; Chawla, C. P.; Chatterton, P. M.; Trapp, M. A.; Chang, C. H.; Griffin, A. C. *Polym. Prepr.* **1988**, *29*(1), 518.
(17) Hoyle, C. E.; Chang, C. H.; Trapp, M. A. *Macromolecules*, submitted for publication.
(18) Latham, D. D.; McLaughlin, K. W.; Hoyle, C. E.; Trapp, M. A. *Polym. Prepr.* **1988**, *29*(2), 328.
(19) Pemberton, D. R.; Johnson, A. F. *Polymer* **1984**, *25*, 529.
(20) Davies, A. K.; Cundall, R. B.; Bate, N. J.; Simpson, L. A. *J. Radiat. Curing* **1987**, *14*(2), 22.
(21) Tanny, G. B.; Lubelsky, A.; Ray-Noy, Z.; Shchori, E. Proceedings of Radcure Conference; Basel, 1985, 85–440.
(22) Small, R. D.; Ors, J. A.; Royce, B. S. *ACS Symp. Ser.* **1984**, *242*, 325.
(23) Decker, C.; Fizet, M. *Makromol. Chem. Rapid Commun.* **1980**, *1*, 637.
(24) Fizet, M.; Decker, C.; Faure, J. *Eur. Polym. J.* **1985**, *21*, 427.
(25) Decker, C. *Radiation Curing of Polymers*; Randell, D. R., Ed.; Royal Society of Chemistry, 1987; No. 64, p 16.
(26) Decker, C.; Moussa, K. *Makromol. Chem.* **1988**, *189*, 2381.
(27) Decker, C. *Makromol. Chem.* **1979**, *180*, 2027.
(28) Aronhime, M. T.; Gillham, J. K. *J. Coat. Technol.* **1984**, *56*, 35.
(29) Sack, R.; Schulze, G. V.; Meyerhoff, G. *Macromolecules* **1988**, *21*, 3347.
(30) Decker, C.; Bendaikha, T. *Eur. Polym. J.* **1984**, *20*, 753.

(31) Decker, C.; Jenkins, A. *Macromolecules* **1985**, *18*, 1241.
(32) Chevallier, F.; Chevalier, S.; Decker, C.; Moussa, K. Proceedings of Radcure Conference; Münich, 1987, 87–9.
(33) Tryson, G. R.; Shultz, A. R. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2059.
(34) Decker, C. *ACS Symp. Ser.* **1984**, *266*, 207.
(35) Decker, C.; Moussa, K. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *25*, 739.
(36) Decker, C.; Moussa, K. *J. Appl. Polym. Sci.* **1987**, *34*, 1603.
(37) Merlin, A.; Fouassier, J. Pp. *J. Chim. Phys.* **1981**, *78*, 267.

Application of Wittig-Type Reactions of Titanacyclobutane End Groups for the Formation of Block and Graft Copolymers

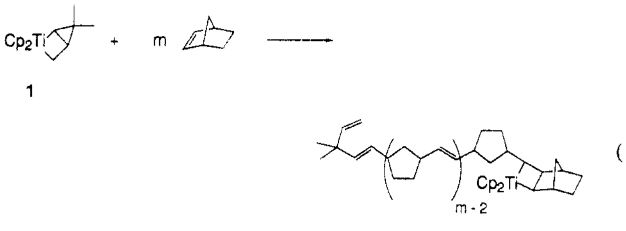
Wilhelm Risse and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis,[†] California Institute of Technology, Pasadena, California 91125. *Received November 18, 1988; Revised Manuscript Received April 13, 1989*

ABSTRACT: Polynorbornene and poly(*exo*-dicyclopentadiene) with one titanacyclobutane end group were linked in a Wittig-type reaction with polymeric ketone groups. The reaction of these living polymers with α,ω-bis(4-benzoylphenyl)poly(oxy-2,6-dimethyl-1,4-phenylene) gave ABA triblock copolymers polynorbornene-*block*-poly(oxy-2,6-dimethyl-1,4-phenylene)-*block*-polynorbornene and poly(*exo*-dicyclopentadiene)-*block*-poly(oxy-2,6-dimethyl-1,4-phenylene)-*block*-poly(*exo*-dicyclopentadiene). Graft copolymers containing polynorbornene side chains were obtained from a reaction with a poly(ether–ketone).

Introduction

Titanium,[1] tungsten,[2] molybdenum,[3] and tantalum[4] complexes have been applied for the living ring-opening olefin metathesis polymerization (ROMP)[5] of norbornene. Bis(η^5-cyclopentadienyl)titanacyclobutane compounds derived from 3,3-dimethylcyclopropene, norbornene, and isobutylene are used as titanium-based initiators[1,6] (eq 1). These initiators produce polymer chains containing a titanacyclobutane end group that is stable at room temperature but is capable of renewed monomer addition when heated above 65 °C. The subsequent addition of different cyclic olefins, such as dicyclopentadiene, benzonorbornadiene, and 6-methylbenzonorbornadiene, resulted in the formation of low-dipersity block copolymers.[7]



1

(1)

2

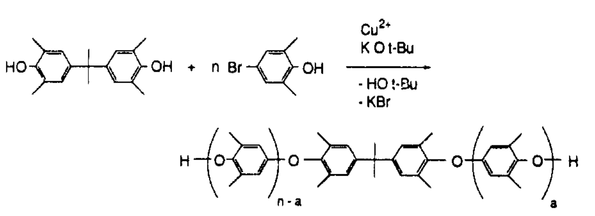
Titanacyclobutanes when heated to the temperature where they cleave to titanium carbene complexes are also known to react with ketones, esters, and amides to form the corresponding olefins, enol ethers, and enamines.[8] Polynorbornene with one diphenylethenyl end group was obtained from the reaction of living polynorbornene with benzophenone.[9]

The present paper describes the application of the Wittig-type reaction for the preparation of block and graft copolymers. Titanacyclobutane structures were used as reactive end groups to link polynorbornene and poly(*exo*-dicyclopentadiene) blocks with polymers containing ketone groups.

Results and Discussion

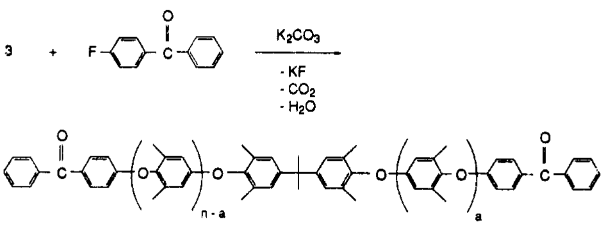
The hard block poly(oxy-2,6-dimethyl-1,4-phenylene)[10] was selected for the synthesis of ABA triblock copolymers with polynorbornene and poly(*exo*-dicyclopentadiene) segments. The oxidative polymerization of 2,6-dimethylphenol and the dehalogenation polymerization of 4-halo-2,6-dimethylphenol give poly(phenylene ethers) with phenolic hydroxyl end groups.[11] In the past, these aromatic end groups have been utilized for the preparation of block copolymers with polyesters,[12] polycarbonates, and poly(ether–sulfones).[13]

α,ω-Bis(4-benzoylphenyl)poly(phenylene ether) 4 of M_n = 4160 (n = 29) was prepared according to eq 2 and 3. A mixture of 4-bromo-2,6-dimethylphenol and 2,2′,6,6′-tetramethyl-4,4′-isopropylidenediphenol (molar ratio = 25) was polymerized in the presence of catalytic amounts of CuCl$_2$ to give poly(phenylene ether) 3[11b] (eq 2). The experimental value of n is slightly higher than the theoretical value, which corresponds to a monomer ratio of 25. This is probably due to the solubility of the low molecular weight species in methanol, the solvent used for precipitating the polymer. The resulting polymer was reacted with a 50 mol % excess of 4-fluorobenzophenone in a nucleophilic substitution reaction (eq 3). The number of aromatic ketone end groups was determined by ^{1}H NMR spectroscopy. For this purpose, the intensity of the signals at δ 7.75, 7.50, 7.44, and 6.80 (aromatic protons of the end groups) was related to the intensity of the signals at δ 6.42 (aromatic protons of the monomer units) (Figure 1). A value of 1.9 was obtained for the number of ketone end groups for polymer 4.



(2)

3



(3)

4

[†] Contribution No. 7887.

0024-9297/89/2222-4462$01.50/0