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Photopolymerization of dialkyl fumarates with electron donor monomers

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Fumarate esters with abstractable hydrogens were found to copolymerize via photoinitiation with a variety of electron donor monomers at a relatively rapid rate both in air and in nitrogen. In air, copolymerization rates of the dialkyl fumarates made from reaction of fumaric chloride with 1-methoxyisopropanol or 2-methoxy-1-ethanol were much faster than for monofunctional or difunctional acrylates when a photoinitiator was used to initiate polymerization. Mixtures involving dialkyl fumarates and *N*-vinylformamide (NVF) had polymerization exotherm rates faster than when *N*-vinylpyrrolidone and vinyl ethers were used as comonomers. Similar correlations with fumarate structure were observed when photoinitiator was present or absent, but faster rates were always obtained when a photoinitiator was present. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: dialkyl fumarates; photopolymerization; electron donor monomers)

INTRODUCTION

The use of light to initiate the polymerization of monomers continues to be an efficient and environmentally safe method for generating cross-linked polymer films for applications ranging from coatings on floors to protective films on optical fibres. New developments have led to the introduction of unsaturated ester–vinyl ether resin mixtures with photoinitiators which are capable of giving cross-linked films upon exposure to high-intensity light[1–6]. Recently, Hall *et al.*[7–11] reported that certain donor–acceptor monomer combinations can polymerize upon exposure to light in the absence of added photoinitiator; it was proposed that initiation of polymerization of such donor–acceptor systems proceeded by excitation of ground-state charge transfer (CT) complexes, presumably forming a diradical species (see *Scheme 1*) capable of initiating polymerization. Indeed, there are many advantages to inducing efficient photopolymerization without added photoinitiator, including elimination of absorbing species in the final polymerized film as well as the reduction in cost associated with the photoinitiator. Since the synthesis of unsaturated esters is economically attractive, it would be advantageous to develop unsaturated ester–comonomer systems which polymerize without the addition of photoinitiator. Alternatively, unsaturated ester–donor monomer mixtures which polymerize rapidly in the presence of added photoinitiator would allow their use in a variety of applications requiring rapid polymerization from which they are currently excluded.

In order to determine the structural parameters which affect the copolymerization rates of unsaturated esters with donor monomers, we initiated an investigation of the photopolymerization efficiency of a series of dialkyl fumarate acceptor monomers and three donor monomers: *N*-vinylformamide (NVF), *N*-vinylpyrrolidone (NVP) and triethyleneglycol divinyl ether (TEGDVE). Results are reported for polymerization in air and in nitrogen, with and without added photoinitiator. The dialkyl fumarate acceptor monomers used in this study are monofunctional and may serve as models for multifunctional ester monomers. The tendency for dialkyl ester–donor monomers to copolymerize via an alternating process is well established in the literature[12–16], and hence is not the subject of the present investigation. This paper considers the effect of the structure of the dialkyl ester and the nature of the donor on the polymerization rate.

EXPERIMENTAL

Materials

Diethyl fumarate was obtained from Aldrich. All other fumarates were prepared by the reaction of fumaric chloride with the corresponding alcohol (see below) and purified by crystallization or distillation under reduced pressure. ^{13}C n.m.r. ($CDCl_3$) spectroscopic characterization follows:

Diethyl fumarate (DEF): 164.77 ($\underline{C}$=0), 133.38 ($\underline{C}H$=), 61.09 ($\underline{C}H_2$), 13.90 ($\underline{C}H_3$).

Di-*n*-butyl fumarate (D*n*BF): 164.92 ($\underline{C}$=O), 133.54 ($\underline{C}H$=), 64.96 ($COO\underline{C}H_2$), 30.38 ($CH_2\underline{C}H_2$), 18.94 ($CH_2\underline{C}H_2CH_3$), 13.57 (CH_3).

Di-*tert*-butyl fumarate (DtBF) (m.p. 66–68°C): 164.41 ($\underline{C}$=O), 134.82 ($\underline{C}H$=), 81.33 ($\underline{C}(CH_3)_3$), 28.33 ($\underline{C}H_3$).

Di(2-methoxyethyl) fumarate (DMEF): 164.96 ($\underline{C}$=O), 133.79 ($\underline{C}H$=), 70.11 ($COO\underline{C}H_2$), 64.33 ($COOCH_2\underline{C}H_2$), 59.14 ($O\underline{C}H_3$).

Di(1-methoxy-2-propyl) fumarate (DMPF): 164.45 ($\underline{C}$=0), 133.88 ($\underline{C}H$=), 74.84 ($COO\underline{C}H_2$), 70.43 ($COOCH_2\underline{C}H_2$), 59.13 ($O\underline{C}H_3$), 16.44 ($\underline{C}H_3$).

Dibenzyl fumarate (DBzF) (m.p. 49–51°C): 164.89

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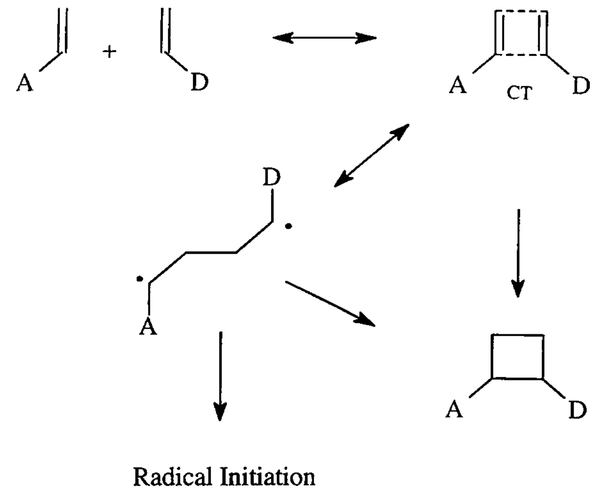


Scheme 1

($\underline{C}$=O), 133.94 ($\underline{C}$H=), 135.41, 128.87, 18.76, 128.57 (Ar), 67.35 (COO$\underline{C}$H$_2$).

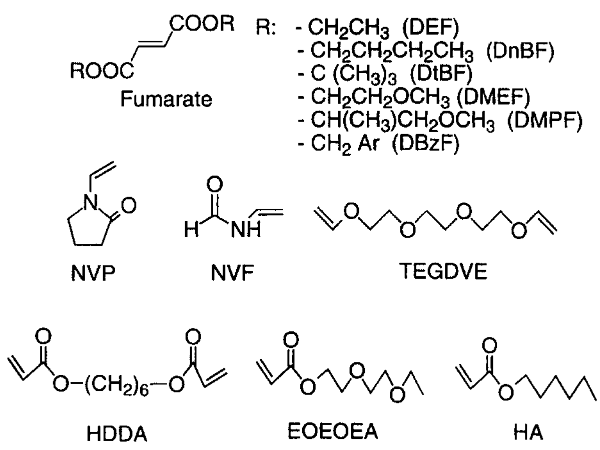
N-vinyl-2-pyrrolidone (NVP) was obtained from Aldrich and purified by distillation at reduced pressure. *N*-vinylformamide (NVF) and triethyleneglycol divinyl ether (TEGDVE) were obtained from Air Products and International Science Products, and were used as received. Hexyl acrylate (HA), 2-(2-ethoxyethoxy)ethyl acrylate (EOEOEA) and 1,6-hexanediol diacrylate (HDDA) were purchased from Aldrich, Thiokol and Polysciences respectively. The photoinitiator (2,2-dimethoxy-2-phenylacetophenone, DMPA) was obtained from Ciba Geigy and used as received.

Instrumentation

The photo-d.s.c. experiments were performed on a modified Perkin-Elmer DSC-2 apparatus equipped with quartz windows, an electrically driven shutter and a medium-pressure mercury lamp (Canrad Hanovia). The light intensity of unfiltered light was between 15 and 23 mW cm^{-2}. In some instances, line filters were used to isolate mercury lines, and neutral density filters were used to reduce the light intensity. Samples (3 mg) were placed in aluminium d.s.c. pans and irradiated at 50°C. U.v.–vis spectra were recorded on a Perkin-Elmer Lambda 6 UV–VIS spectrophotometer using cells of 1 cm path length.

RESULTS AND DISCUSSION

Results are first given for the photoinitiated polymerization of several fumarate esters with a representative donor, *N*-vinylformamide (NVF). By comparing rates of polymerization for several fumarate ester–NVF combinations with acrylate monomers using photoinitiators, a reliable assessment of the relative efficiency of fumarate ester–NVF systems can be obtained. Comparison of results of polymerization in nitrogen and air provides a means of predicting the performance of actual u.v. curing processes which may be conducted in air. The data are interpreted in the light of the availability of abstractable hydrogen in the fumarate ester acceptor monomers. Results are then given for dialkyl fumarates with other donors. The structures of the fumarate ester monomers, the three donor monomers and the acrylate monomers used in this investigation are given below for reference.



Exotherms of dialkyl fumarate–NVF systems with photoinitiator

To determine first the relative inherent polymerization rates of fumarate ester–NVF acceptor–donor systems, care was taken to ensure that only the added photoinitiator (1 wt% DMPA) absorbed light. A bandpass filter was used to isolate the 366 nm line of the medium-pressure mercury lamp, which was directed to the sample and reference pans of a DSC-2, modified as described in Experimental. The resulting exotherms are shown in *Figure 1* for three fumarate ester–NVF systems in nitrogen, along with exotherms for two monofunctional acrylates (HA and EOEOEA) and a difunctional acrylate (1,6-hexanediol diacrylate, HDDA). It is quite obvious that HDDA has the greatest exotherm. This is to be expected, since it is a difunctional monomer which is known to polymerize via a rapid inhomogeneous network process[17,18]. What is

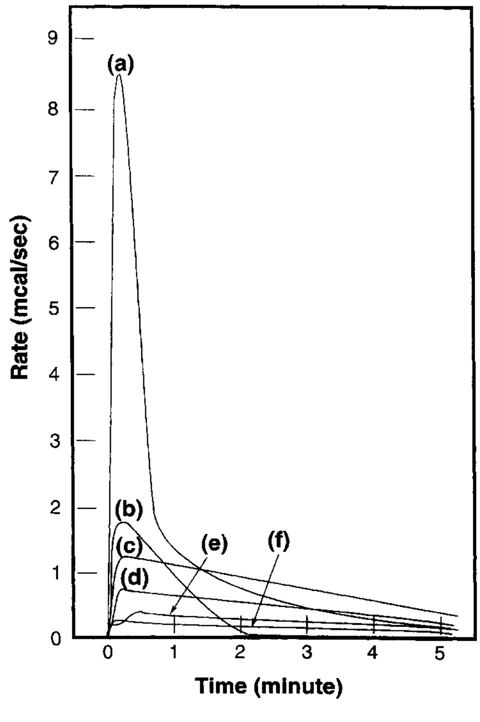


Figure 1 Exotherms in nitrogen of the photoinitiated polymerization of samples with 1 wt% DMPA using the 366 nm output (0.005 mW cm^{-2}) of a medium-pressure mercury lamp: (a) HDDA; (b) DMPF–NVF; (c) EOEOEA; (d) DEF–NVF; (e) HA; (f) DBzF–NVF. All mixtures are equimolar

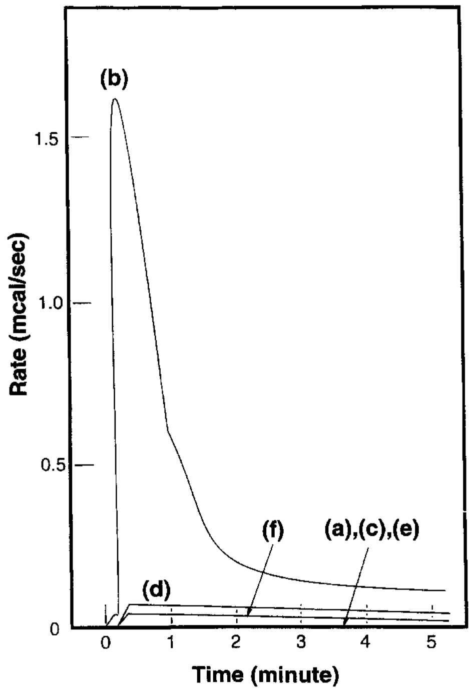


Figure 2 Exotherms in air of the photoinitiated polymerization of samples with 1 wt% DMPA using the 366 nm output (0.05 mW cm^{-2}) of a medium-pressure mercury lamp: (a) HDDA; (b) DMPF–NVF; (c) EOEOEA; (d) DEF–NVF; (e) HA; (f) DBzF–NVF. All mixtures are equimolar

Table 1 H_{max} of dialkyl fumarate–NVF mixtures with photoinitiator

Dialkyl fumarate	H_{max} (mcal s^{-1})	
	Nitrogen[a]	Air[b]
DEF	0.68	0.09
D*n*BF	0.80	0.10
D*t*BF	0.27	0.05
DMEF	1.00	1.53
DMPF	1.82	1.75
DBzF	0.22	0.05

[a] Intensity of light source at 366 nm: 0.005 mW cm^{-2}

[b] Intensity of light source at 366 nm: 0.05 mW cm^{-2}

somewhat unexpected is the polymerization rate of DMPF–NVF and DEF–NVF compared with pure HA. By comparing exotherm peaks, it can be concluded that NVF with both DMPF and DEF polymerizes at a greater rate than the monofunctional acrylate HA. The high efficiency for the DMPF–NVF system may be partly a result of the presence of abstractable hydrogens. In support of this hypothesis, it is found that EOEOEA, which is an acrylate comparable with HA but with ether linkages and hence abstractable hydrogens, polymerizes significantly faster than HA.

Interestingly, it might be expected that the presence of ether functional groups, which provide a means for chain transfer (via hydrogen abstraction) and subsequent gelation, might result in an unusually rapid rate (comparatively) for polymerization conducted in the presence of oxygen. After all, it is well known that the resistance of difunctional and trifunctional acrylates to oxygen inhibition is greater than for monofunctional acrylates, presumably due to the formation of microgels early in the polymerization process. The DMPF should have a high propensity for formation of a gel at low conversions, due to the combination of a reactive double bond and two side-chain branches where hydrogen abstraction can occur, i.e. each DMPF monomer has the possibility of reaction at three positions. In accordance with expectation, *Figure 2* shows that the rate of polymerization of DMPF–NVF in air is much faster than for any of the other fumarate ester–NVF systems or even the acrylate-based systems. Interestingly, it was observed that DMPF–NVF polymerization both in nitrogen and in air forms highly cross-linked networks, whereas the other monofunctional systems did not. Although HDDA forms a cross-linked network, it did not exhibit a fast polymerization rate in air under the light intensity used. *Table 1* gives values of the peak exotherm maxima H_{max} for polymerization of all the dialkyl fumarates investigated in air and nitrogen. It is noted that the only monomer in addition to DMPF to exhibit a high rate in air is DMEF, which, like DMPF, has two ester groups with abstractable hydrogens.

The relatively low resistance to oxygen quenching exhibited by HDDA compared with DMPF–NVF, or even DEF–NVF and DBzF–NVF for that matter, may be due to a variety of reasons, including the absence of abstractable

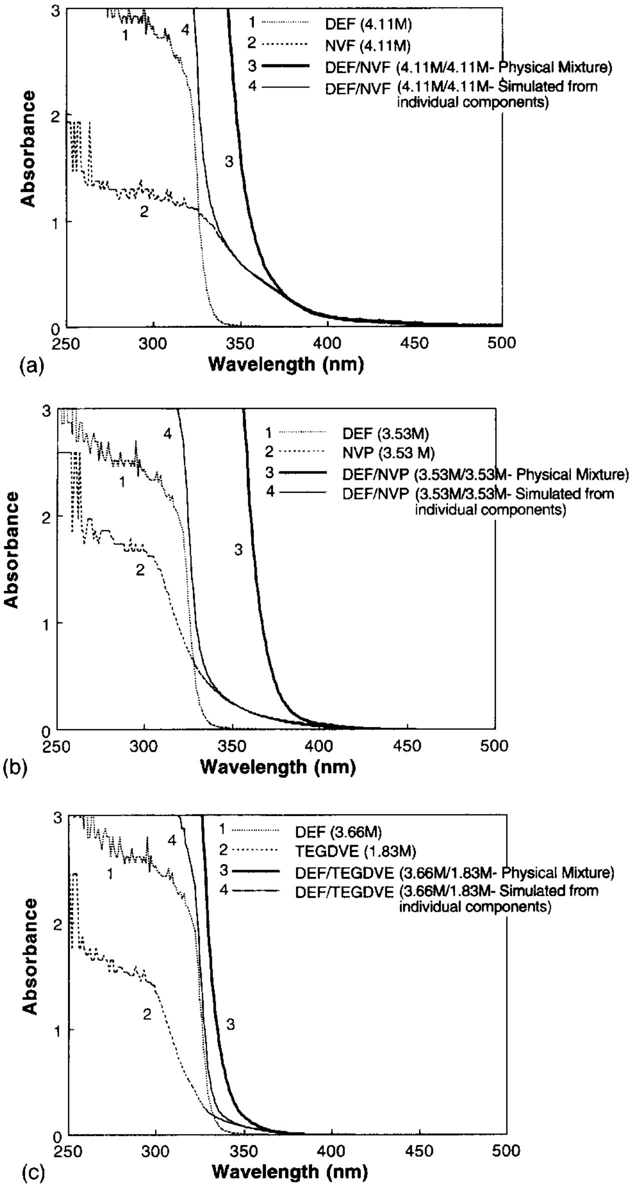


Figure 3 U.v. absorption spectra of (a) DEF and NVF systems as indicated, (b) DEF and NVP systems as indicated, and (c) DEF and TEGDVE systems as indicated

hydrogens, as well as a higher susceptibility to the reaction between acrylate-derived radicals and oxygen. Indeed, it as has been suggested previously[10,12] that systems in which monomers form ground-state charge transfer (CT) complexes experience diminished susceptibility to quenching of the polymerization by reaction of chain ends with oxygen.

In the next subsection it is shown that both NVF and other donor monomers form CT complexes with unsaturated ester monomers. Hence the relative insensitivity of NVF–unsaturated ester mixtures to oxygen may be inherent to the formation of CT complexes in these systems. However, additional work is required to substantiate the origin of the oxygen effect in these systems.

U.v. absorption spectra

To determine the existence of ground-state CT complexes between fumarate esters and electron donor monomers such as NVF, the absorption spectra of the pure components (fumarate ester and NVF) were compared with those of physical mixtures of the two monomers. Results are presented here for a mixture of NVF and diethyl fumarate (DEF); similar results were obtained for NVF with the other fumarate esters. *Figure 3a* shows absorption spectra for 4.11 M DEF (curve 1), 4.11 M NVF (curve 2) and a mixture of 4.11 M DEF and 4.11 M NVF (curve 3). For comparison, a composite spectrum made by adding point by point the absorbance of 4.11 M DEF and 4.11 M NVF is also given (curve 4—corrections made for second component). Comparison of curves 3 and 4 makes it obvious that the physical mixture (curve 3) exhibits enhanced absorption at wavelengths between 330 and 350 nm. This suggests the formation of a CT complex between DEF and NVF. In anticipation of results in the next subsection, absorption spectra are also shown in *Figure 3b* and *c* corresponding to mixtures of DEF and *N*-vinylpyrrolidone (NVP) and DEF and tetraethyleneglycol divinyl ether (TEGDVE). Since both NVP and TEGDVE are also electron donors, it might be expected that DEF–NVP and DEF–TEGDVE mixtures would exhibit a distinctly red-shifted absorption spectrum compared with the simple addition of the individual absorbances. Indeed, *Figure 3b* and *c* show that both TEGDVE and NVP form CT complexes with distinctly red-shifted absorption bands. Although we have not resolved the relative importance of the equilibrium complex concentration and the complex extinction coefficient for any of the systems depicted in *Figure 3*, the pronounced red-shifts in the absorption spectra indicate that a CT complex is definitely formed in concentrations large enough to be recorded by u.v. absorption spectroscopy.

Exotherms of dialkyl fumarate–NVF systems without photoinitiator

Since NVF forms a CT complex with dialkyl fumarates, it was of interest to see whether polymerization could be initiated photolytically without added photoinitiator (as in *Figures 1 and 2*). Little detectable polymerization could be obtained for any NVF–dialkyl fumarate system when the filtered 366 nm source was used. This arises from the poor absorbance at 366 nm by the systems without added photoinitiator. To ensure therefore that the light source included wavelengths of high-enough energy to initiate the polymerization of the photoinitiatorless NVF–dialkyl fumarate mixtures, the bandpass filter was removed and the samples were exposed to the unfiltered output of the medium-pressure mercury lamp.

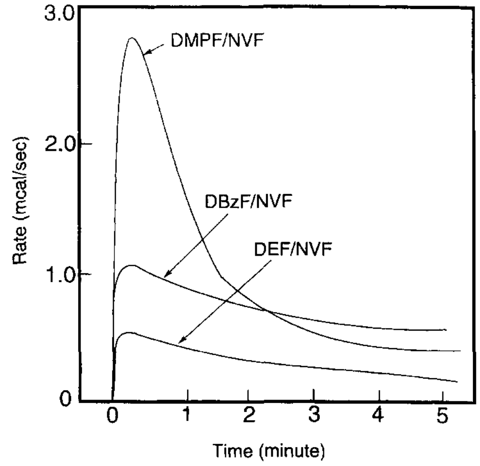


Figure 4 Exotherms of the photoinitiated polymerization of equimolar mixtures of DMPF, DEF and DBzF with NVF in nitrogen using the unfiltered output (15–17 mW cm^{-2}) of a medium-pressure mercury lamp

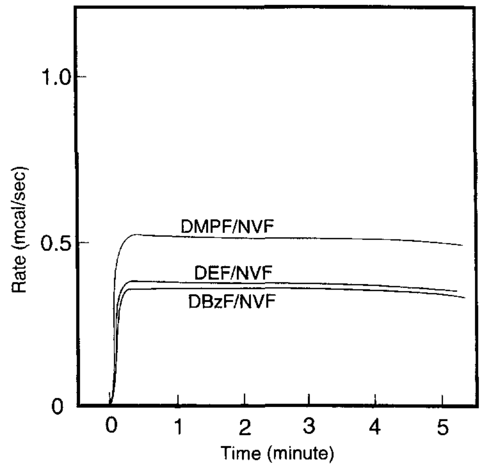


Figure 5 Exotherms of the photoinitiated polymerization of a equimolar mixture of DMPF, DEF and DBzF with NVF in air using the unfiltered output (15–17 mW cm^{-2}) of a medium-pressure mercury lamp

Figures 4 and 5 show corresponding exotherms for the photoinitiated polymerization of three equimolar mixtures of NVF–dialkyl fumarate. As in the polymerization of these systems with photoinitiator present, *Figures 4 and 5* show that the DMPF–NVF exotherms are substantially greater than for DEF–NVF and DBzF–NVF exposed to comparable light intensities in nitrogen (*Figure 4*) and in air (*Figure 5*) atmospheres. *Table 2* shows the peak exotherm maxima (H_{max}) for each of the dialkyl fumarates with NVF and no photoinitiator. From the exotherm curves in *Figures 4 and 5* and the H_{max} values in *Table 2*, it is obvious that, as in the cases where added photoinitiator was used (*Figures 1 and 2* and *Table 1*), the dialkyl fumarates DMPF and DMEF with readily abstractable hydrogens yield the fastest copolymerization rates with NVF. In the present case for photopolymerization of NVF–dialkyl fumarate mixtures without photoinitiator, the rates in nitrogen are much greater for the DMPF–NVF and DMEF–NVF mixtures, while the differences between rates for dialkyl fumarate–NVF mixtures in air are not as great as in nitrogen. This is interesting in view of the markedly greater polymerization rate maxima found for DMPF–NVF and DMEF–NVF systems where an added photoinitiator was used. We suspect that there may be differences in the relative

Table 2 H_{max} of dialkyl fumarate–NVF mixtures with no photoinitiator[a]

Dialkyl fumarate[b]	H_{max} (mcal s^{-1})	
	Nitrogen	Air
DEF	0.65	0.39
D*n*BF	0.95	0.21
D*t*BF	0.76	0.41
DMEF	1.55	0.40
DMPF	2.70	0.52
DBzF	1.09	0.37

[a] Light intensity 15–17 mW cm^{-2}

[b] Equimolar mixtures of NVF with the appropriate dialkyl fumarate

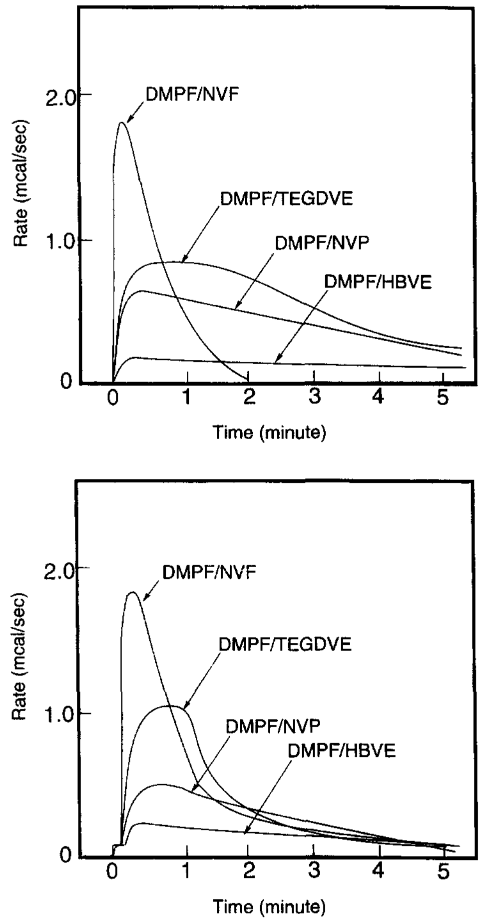


Figure 6 Exotherms of the photoinitiated polymerization of equimolar mixtures of DMPF with various electron donors with 1 wt% DMPA using the 366 nm output of a medium-pressure mercury lamp in (a) nitrogen (output 0.005 mW cm^{-2}) and (b) air (output 0.05 mW cm^{-2})

initiation rates of donor–acceptor systems in the presence of oxygen in cases where no photoinitiator is used; however, at present we have no conclusive explanation for the failure of photoinitiatorless DMPF–NVF and DMEF–NVF systems to attain substantially higher maxima in air under the conditions used.

Comparison of exotherms of dialkyl fumarate–electron donor systems

Here the relative efficiency of three electron donors with dialkyl fumarates is analysed. The results in *Figure 3* suggested that NVF, NVP and TEGDVE all form CT complexes with dialkyl fumarates. *Figure 6a* and *b* show exotherms for the photopolymerization of DMPF with NVF, NVP, 1-hydroxybutyl vinyl ether (HBVE) and TEGDVE.

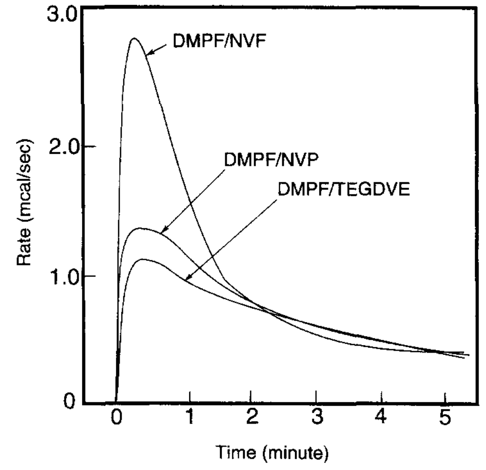


Figure 7 Exotherms of the photoinitiated polymerization of equimolar mixtures of DMPF with NVF, NVP and TEGDVE in nitrogen using the unfiltered output (15–17 mW cm^{-2}) of a medium-pressure mercury lamp

Table 3 H_{max} of fumarates with various electron donor comonomers

Combination[a]	H_{max} (mcal s^{-1})[b]	
	N_2	Air
DEF–NVP	0.74	0.38
DEF–NVF	0.65	0.39
DEF–TEGDVE	0.63	0.41
D*n*BF–NVP	0.73	0.25
D*n*BF–NVF	0.95	0.21
D*n*BF–TEGDVE	0.55	0.28
D*t*BF–NVP	0.50	0.36
D*t*BF–NVF	0.76	0.41
D*t*BF–TEGDVE	0.48	0.42
DMEF–NVP	1.17	0.35
DMEF–NVF	1.55	0.40
DMEF–TEGDVE	1.17	0.38
DMPF–NVP	1.37	0.53
DMPF–NVF	2.70	0.52
DMPF–TEGDVE	1.10	0.51
DBzF–NVP	0.62	0.31
DBzF–NVF	1.09	0.37
DBzF–TEGDVE	0.66	0.33

[a] Equimolar concentrations of each double bond

[b] Light intensity 15–17 mW cm^{-2}

Although the DMPF–NVP exotherm was substantially higher than the DMPF–HBVE exotherm, it was clearly much lower both in nitrogen and in air than the DMPF–NVF exotherm. At this point in the investigation, it is not possible to draw a clear correlation between the extent of CT formation and the rate of polymerization attained when a common photoinitiator is used, since no data are available on equilibrium concentrations of CT complexes. All that can be concluded is that all three systems involving the electron donors HBVE, NVP and NVF result in polymerization with differences which appear to have no direct correlation with the extent of the red-shift in the absorption spectrum of the CT complex formed. One final observation is that the exotherms in *Figure 6a* and *b* for DMPF–HBVE, where both monomers are monofunctional, are substantially lower than for DMPF–TEGDVE, where the ether donor monomer is difunctional. This is reasonable in view of Kloosterboer's results on microgel formation and the resulting rate increase of difunctional acrylate monomers[17,18].

When equimolar samples of DMPF with NVP, NVF and TEGDVE (without added photoinitiator) were exposed to the unfiltered output of the medium-pressure mercury lamp, the polymerization exotherms indicated reasonable rates for each system (*Figure 7*). As in the case where a photoinitiator was used, the exotherm maximum was greatest for the DMPF–NVF mixture. *Table 3* is a full compilation of $H_{\max}$ results for the exotherms of all the photoinitiatorless dialkyl fumarate mixture with NVP, NVF and TEGDVE (monofunctional vinyl ethers were not used, since the exotherms were too low to obtain reliable measurements). As for DMPF (*Figure 7*) in nitrogen, all the dialkyl fumarates except DEF exhibited essentially the same relative order of reactivity with the three donors, i.e. the systems with NVF had substantially greater rates than those with NVP or TEGDVE in nitrogen. The results for polymerization in the presence of air are more difficult to interpret. As discussed previously, the exotherms in air show relatively small differences among the various dialkyl fumarate–NVF mixtures, i.e. the results for NVP, NVF and TEGDVE in air are essentially identical for any one dialkyl fumarate. For example, the peak maxima ($H_{\max}$) for DMPF with NVP, NVF, and TEGDVE are 0.53, 0.52 and 0.51 mcal s^{-1}. It may be that in each case oxygen effectively inhibits the generation of primary radicals. Since the initiation process may well be via excitation of a CT complex and subsequent collapse to a biradical initiating species, it would seem feasible that oxygen could quench the excited CT complex at a diffusion-controlled rate. Other explanations for the 'levelling' effect of oxygen may be valid, but a definitive explanation is postponed to a future investigation.

CONCLUSIONS

The photoinitiated polymerization of a variety of dialkyl fumarate–electron donor monomer systems has been investigated. Dialkyl fumarates with readily abstractable hydrogens yielded the fastest copolymerization rates in air and nitrogen with *N*-vinylformamide, *N*-vinylpyrrolidone and divinyl ether monomers. Systems where *N*-vinylformamide was the donor gave the highest rates of polymerization. CT complexes were formed between all three donors and dialkyl fumarates. Low but measurable rates of polymerization were obtained upon exposure of systems with no photoinitiator. Results will be presented in the future showing that certain multifunctional ester acceptor monomer–electron donor mixtures exhibit acceptable u.v. curing rates on exposure to traditional high-intensity u.v. curing lamp sources.

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