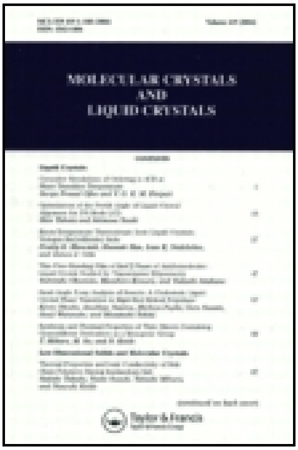

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Copolymerization by Gamma-Irradiation of Eutectic Mixtures

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Abstract—Experimental work was concentrated on attempts to prepare copolymers from solid binary eutectics. Styrene and β-propiolactone were investigated as an example of a system comprising a vinyl and a cyclic monomer. Only a mixture of homopolymers was obtained as a result of γ-irradiation and, more generally, it is maintained that convincing evidence of copolymerization in such systems has not been presented in the scientific literature.

Attention was also given to a number of binary mixtures of monomer to find eutectic mixtures which are solid at room temperature and which, therefore, can be examined conveniently by physical techniques for determining the structure of a solid. A high yield of copolymer, up to 60% conversion of the eutectic mixture, was obtained from the system, N-vinyl carbazole/N-phenyl acrylamide. Rather surprizingly, thermal gravimetric analysis indicated that the monomer units were distributed at random in the copolymer rather than in blocks. This would seem to imply a system in which the two types of monomer unit are intimately mixed and so would appear inconsistent with the view that the eutectic comprises separate crystals of each monomer. Alternatively, the findings can be explained more plausibly as being due to copolymerization in a glass and this was borne out by examination of the freshly solidified melt. The glassy state persisted for several hours at room temperature but then crystallization became noticeable. After several days large crystals (10–100μ) had grown and when the system was irradiated in this state only a mixture of homopolymers was formed.

1. Attempted Copolymerization of Vinyl and Cyclic Monomers

There has been considerable interest in recent years in the copolymerization of various monomer pairs in the crystalline state.[1] Such studies

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contribute to our knowledge of solid state reactions and also might lead to copolymers of unusual composition and sequence distribution. Comparatively few organic compounds form solid solutions whereas eutectic compositions are much more generally encountered. In general, most examples of copolymerization in the crystalline state have involved either cyclic–cyclic monomer pairs or pairs of vinyl monomers. Only a few examples of solid mixtures of a vinyl and a cyclic monomer have been reported. Such mixtures appear *a priori* to be discouraging since cyclic compounds tend to polymerize topotactically and vinyl compounds in some other manner. However, Okamura, Hayashi, and Kitanishi have reported that exposure of mixtures of acrylonitrile and β-propiolactone (and, also, acrylonitrile and diketene) to electrons or γ-rays at − 78 °C results in the formation of a copolymer.[2,3] Their criterion for copolymer formation, however, appears inadequate, being that the polymeric product was insoluble in hot dimethyl formamide which dissolves both polyacrylonitrile and poly-β-propiolactone. However, more convincing evidence for the presence of blocks of each polymer in the polymeric product was adduced from X-ray diffraction and melting point data. In further commentary on this report it must be noted that as the melting point of acrylonitrile is − 83.5 °C, this example is for a case in which only the cyclic monomer is present in the solid state. Nevertheless, if the report is correct it would be interesting because of its implication that the polymerization of a solid cyclic monomer is not entirely restricted to its own lattice.

The present work is concerned with the question of whether copolymers can be prepared by γ-irradiation of solidified mixtures of vinyl and cyclic monomers and, if so, to elucidate the factors which make for success. The latter aim is more likely to be realized if the physical state of the binary system is known. Preliminary experiments showed that a well-defined phase diagram could be established for styrene and β-propiolactone and, therefore, this binary system was studied first.

Experimental

Commercial samples of acrylonitrile, styrene, and β-propiolactone were purified and dried by up to three distillations in vacuo over calcium hydride. Mixtures of acrylonitrile and β-propiolactone were made up in vacuo in flamed glassware. Mixtures of styrene and β-propiolactone were made up by two techniques. In the first, the dried monomers were briefly exposed to air and moisture before degassing and sealing in vacuo in ordinary glassware In the second, supper-dried mixtures were prepared from styrene which had been distilled in vacuo over benzophenone and sodium onto previously baked silica gel and from β-propiolactone which had been distilled in vacuo over calcium hydride onto baked silica gel. The glassware used in this second procedure had been dried by repeated washings with benzene dried over benzophenone and sodium and, finally, flamed in vacuo (cf. ref. 4).

Mixtures were either shock cooled to – 196 °C by immersion in liquid nitrogen, or cooled gradually to the temperature of irradiation. Samples were exposed to Co-60 γ-rays at a dose rate of 0.16 Mrad/min. Immediately after irradiation the tubes were opened to the air and the contents leached with hot methanol to remove unreacted monomer. Characterization of the polymeric products is described below.

The phase diagram of the styrene and β-propiolactone system was determined by differential scanning calorimetry measurements.

RESULTS AND DISCUSSIONS

A phase diagram shows that a eutectic with a melting point of – 51°C is formed by a mixture of styrene: β-propiolactone : : 55 : 45 (Fig. 1.) Such mixtures were irradiated just below the melting point, i.e. at – 53 ± 1°C, as this is expected to favor a maximum rate of polymerization in the solid state. The cooling procedure, prior to irradiation, had a drastic influence on the yield of polymer which was one order of magnitude lower for gradually cooled than for shock-cooled samples (Fig. 2). The yield was also less, by about one-half, if shock-cooled samples were not superdry. For comparison, yields of polymer from shock-cooled samples of dry (but not super-dry) monomers irradiated singly were as follows: β-propiolactone, 15.8% (0.67 Mrad) and 12.6% (3.0 Mrad). styrene, 0.6% (3.0 Mrad).‡

‡ " It is generally the case in the solid state polymerization of cyclic monomers that the conversion to polymer eventually levels off with increasing dose. In the present work this seems to be the case for a dose < 1 Mrad and the somewhat lower conversion at the higher dose (3.0 Mrad) is considered to be within experimental error."

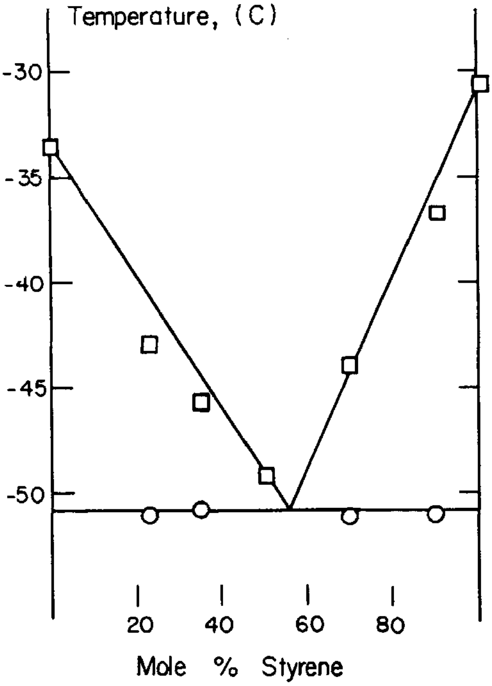

Figure 1. Phase diagram of styrene and β-propiolactone. Precision of temperature measurement: ± 0.5 °C. Heating rate 2.5 °C/min.

Preliminary analysis of made-up mixtures of these homopolymers showed that complete separation could be achieved by precipitation of poly-β-propiolactone from chloroform solution by drop-wise addition of cyclohexane. A preliminary analysis of the super-dry shock-cooled sample designed as *A* in Fig. 2 indicated that a mixture of homopolymers was present; poly-β-propiolactone $>72\,\%$ and polystyrene $> 9\%$. A quantitative analysis of the sample designated as *B* was achieved subsequently viz. poly-β-propiolactone 89% and polystyrene 11% By constrast, all the gradually cooled super-dry samples were found to consist only of polystyrene. Polymers prepared from the dry samples were not analyzed.

The yields of polystyrene alone and in the eutectic mixture are summarized in Table 1. It can be seen that the yield is about 50% higher in the eutectic than alone, even when the mixture was gradually cooled and the pure styrene shock cooled and more than twice as high when the mixture was shock cooled. By contrast the yield of poly-β-propiolactone was markedly reduced in the presence of styrene especially at low doses as may be seen by comparison of the results in Fig. 2 with the yield of 15.8% obtained after a dose of

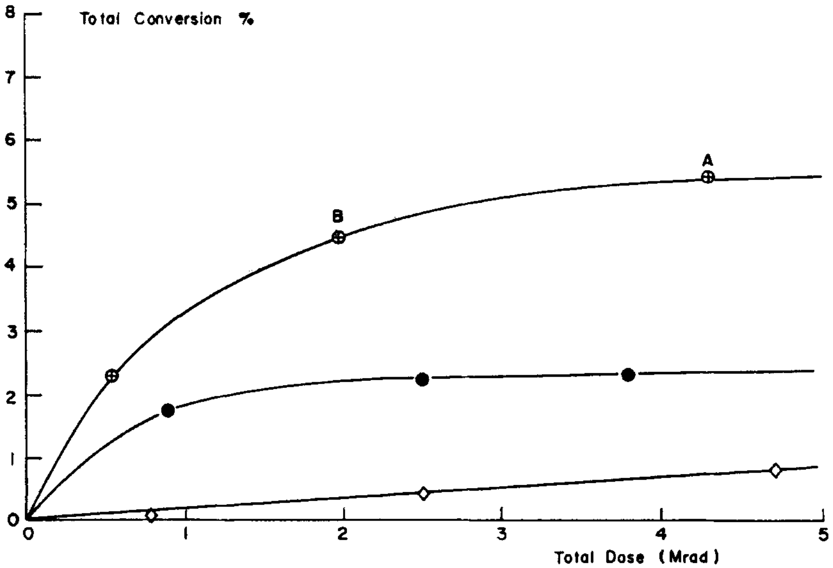

FIG. 2

Figure 2. Total conversion versus dose. Eutectic monomer composition 55 mole % styrene. Temperature of irradiation: − 53 °C. ⊕—Super-dry mixture, shock-cooled at − 196 °C; ●—Dry mixture, shock-cooled at − 196 °C; ◇—Super-dry mixture, gradually cooled at − 53 °C.

TABLE 1 Conversion of Styrene to Polystyrene

System	Dose (Mrad)	% Gross Polymer	% Polystyrene in Gross Polymer	% of Styrene Polymerized	% Per Mrad
Styrene, dry and shock cooled	3.0	0.6	100	0.6	0.20
Mixture, super-dry and gradually cooled	2.5	0.4	100	0.7	0.28
Mixture, super-dry and gradually cooled	4.7	0.8	100	1.5	0.32
Mixture, super-dry and shock cooled	2.0	4.4	11	0.9	0.45

0.7 Mrad when β-propiolactone was irradiated alone. As an extreme case, β-propiolactone did not polymerize at all in the gradually cooled super-dry mixture. Previously, the mutual influence of vinyl and cyclic monomers on rate of polymerization was studied in the case of acrylamide and trioxane, which form an eutectic mixture. Similar results were found in that the rate of polymerization of trioxane was decreased while the rate of polymerization of acrylamide was increased.[5] Confining comments to the cyclic monomers, these results may be rationalized by reference to the finding of Okamura *et al.* that polymerization occurs less efficiently in smaller crystals. It is to be expected that very small crystals would be formed in an eutectic mixture and reasonable to expect that the efficiency of polymerization would be correspondingly small. As to the smaller differences observed when liquid eutectic mixtures are variously cooled, it would be interesting to know whether these too can be correlated with crystal size. This might be checked by X-ray diffraction measurements of crystal grain size (cf ref. 6) but such a study would be more convenient with an eutectic which has a melting point above room temperature. One final feature of the efficiency of polymerization which seems important, is the adverse influence of traces of moisture. If the polymerization mechanism is ionic the adverse effect of moisture is understandable. In any case any additive which interferes with the perfection of crystal formation is known to lead to lower yields in the case of cyclic monomers and water may well be involved in this manner.

From the present point of view, the major point of interest in the above results is that no copolymer was formed under what are presumed to be optimal physical conditions in a solid binary system i.e. where the monomers have a maximum interface and where the mobility in the solid state is maximum. Of course, this leaves unexplored the possibility that copolymerization might occur in other systems especially on account of favorable differences in chemical reactivity. In fact, there are the indications mentioned earlier that this might be the case in the system acrylonitrile and β-propiolactone. Therefore, although the melting point of acrylonitrile seems inconveniently low for establishing a phase diagram, some further experiments were made on the reactivity of an arbitrarily chosen composition, containing a 0.6 mole fraction of acrylonitrile, in both liquid (– 78 °C) and solid (– 120 °C) states. The polymeric products were thoroughly extracted with hot chloroform and the extracted material was shown, by infra-red analysis, to consist of poly-β-propiolactone free of polyacrylonitrile. The insoluble residue was shown, also by infra-red analysis, to contain both poly-β-propiolactone and polyacrylonitrile. As repeated extraction with hot chloroform did not affect the infra-red band intensities it is concluded that this residue consists of a copolymer of the two monomers and, possibly, some homopolymer of acrylonitrile. Details of the experiments are summarized in Table 2.

TABLE 2 Polymeric Products Obtained by γ-Irradiation of Acrylonitrile and β-Propiolactone

			Composition of Polymeric Product	
Temperature of Irradiation	Dose (Mrad)	% Polymerization	% Poly-β-Propiolactone	% Copolyfer (+ any Polyacrylonitrile)
– 78 °C	0.66	2.8	68	32
– 120 °C	3.0	2.7	16	84

The results in Table 2 confirm the report that a copolymer is formed at – 78 °C and, additionally, show that one is also formed at – 120 °C i.e. when both monomers are in the solid stat:. An interesting difference between the products is that the one obtained at – 120 °C is completely soluble in dimethyl formamide whereas the other obtained at – 78 °C is insoluble, comprising crosslinked particles which are highly swollen by both hot dimethyl formamide and hot chloroform. If the insoluble product described previously by Okamura *et al.*[2] as insoluble in dimethyl formamide was, likewise, crosslinked then their criterion for copolymer formation would appear to be satisfactory. Samples of acrylonitrile were irradiated alone to check whether a crosslinked network would be formed. This was not the case, but some observations were made concerning differences of infra-red absorption. The infra-red spectrum of polyacrylonitrile prepared at – 78 °C included a band at 2030 cm^{-1} which was about one-third as intense as the nitrile stretching band at 2250 cm^{-1}. The presence of this band was observed previously in similar experiments and assigned to keteneimine structures

(C=C=N—).[7] However, this band was very weak (less than one-tenth the intensity of the 2250 cm^{-1} band) in the polyacrylonitrile prepared at − 120 °C and also in the copolymers prepared at both − 78°C and − 120 °C. Previously, it was noted that this band was weak in polyacrylonitrile prepared at − 196 °C.[8]

There is good evidence that keteneimine groups are formed by reactions which terminate the mutual growth of two polyacrylonitrile molecules.[8] The relatively low concentrations of such groups in the copolymers prepared in the present work would be consistent with a prior reaction with β-propiolactone which then leads to block polymer formation.

In summary, γ-irradiation of eutectics of styrene and β-propiolactone results in the formation of a mixture of homopolymers only. On the other hand, solid mixtures of acrylonitrile and β-propiolactone yield a copolymer. Further work is desirable in the latter system to establish its physical state prior to irradiation and also to characterize more fully the polymeric products.

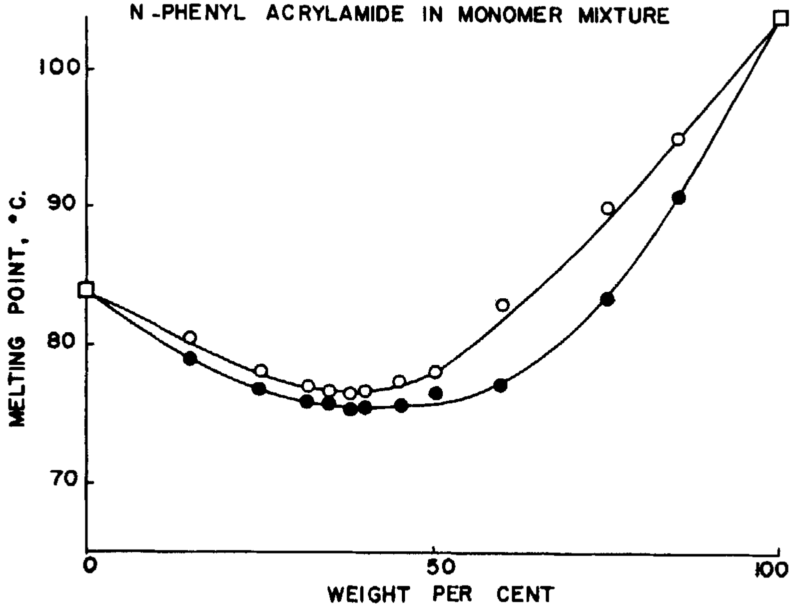

Figure 3. Phase diagrams of N-phenyl acrylamide and N-phenylmethacrylamide. ○—liquidus; ●—solidus.

2. Screening of Binary Systems of Solid Unsaturated Monomers

Binary mixtures of laboratory reagent grade unsaturated monomers which are solid at room temperature were melted, degassed, and sealed in a vacuum. Results obtained following γ-irradiation in the solid state, at an ambient temperature of *ca.* 30 °C, are shown in Table 3; the per cent polymerization refers to material which could not be extracted by methanol, which is a solvent for all the monomers. It will be seen that 11 couples yield large amounts of polymer (60–95%). In each case, one or both of the monomers polymerize readily when irradiated alone in the solid state viz. acrylamide, N-vinyl carbazole, N-vinyl succinimide, and N-phenyl-acrylamide (acenaphthalene also polymerizes alone but higher doses are needed). Generally, couples which do not yield such large amounts of polymer

TABLE 3 Total Polymerization (per cent)

Monomer mixtures 50 wgt. %, except Ac.N + AA: 87 mole % – eutectic compositi
Polymerization temperatures 20 °C or 45 °C
Dose—3 Mrad

	Ac.N	A.A.	F.N.	N.V.C.	N-ϕ-M.A.A.	N-ϕ-A.A.	T.S.	FAME	N.V.S.I
Ac.N		93	0.9	2	0	1.8	1.8	2	
A.A.	93		56	95	60	90	74	~80	
F.N.	0.9	56		49	0	0	0	0	
N.V.C.	2	95	49		Monomers react together on heating	86	63	26	83
N-ϕ-M.A.A.	0	60	0	Monomers react together on heating		80	0	0	59
N-ϕ-A.A.	1.8	90	0	86	80		41	49	
T.S.	1.8	74	0	63	0	41		0	
FAME	2	~80	0	26	0	49	0		
N.V.S.I.				83	59				

		M.P.			M.
Acenaphthylene	(Ac.N)	92°	N-phenyl methacrylamide	(N-ϕ-M.A.A.)	
Acrylamide	(A.A.)	86°	N-phenyl acrylamide	(N-ϕ-A.A.)	1
Fumaronitrile	(F.N.)	96°	Transstilbene	(T.S.)	1
N-vinyl carbazole	(N.V.C.A.)	64°	Fumaric acid monoethyl ester	(FAME)	
			N-vinyl succinimide	(N.V.S.I.)	

include monomers which do not polymerize when irradiated alone viz. fumaronitrile, trans-stilbene.

Phase diagrams were obtained, using recrystallized monomers, for the following systems: N-phenylacrylamide/N-phenylmethacrylamide and N-vinyl carbazole/N-phenylacrylamide. The first of these forms a solid solution (Fig. 3) and the second a eutectic mixture which is discussed in detail in Section 3.

3. Copolymerization of N-Vinyl Carbazole and N-Phenyl Acrylamide

It is not difficult to understand that copolymerization might occur in a solid solution,[9,10] but reports that such a reaction can also occur in eutectic mixtures seem puzzling when considered in conjunction with the belief that such mixtures comprise separate crystals of each monomer. One suggestion made to account for the formation of a copolymer on γ-irradiation of a eutectic mixture of N-vinyl succinimide and N-vinyl pyrrolidone, at a few degrees below the melting point, is that the crystals are exceedingly small and that copolymerization occurs at interfaces.[11] Under similar conditions γ-irradiation of eutectics of maleic anhydride and acenaphthalene was found to yield a one to one alternating copolymer and this indication of intimate mixing evoked the postulate that copolymerization occurs in a liquid-like state at boundaries between the two types of crystals.[12] Subsequently, ample evidence has been presented that copolymers may indeed be formed by γ-irradiation of eutectic mixtures but, as far as is known, no further explanations have been offered to explain how this might occur.[13,14]

The present approach towards answering the question of how two monomers can meet to form a copolymer in a eutectic has been to screen a number of binary mixtures of monomers to find eutectic mixtures which are solid at room temperature and which, therefore, can be examined conveniently by physical techniques for determining the structure of a solid. Such mixtures were additionally screened to identify those which provide a high yield of copolymer because in such a case it would seem more pertinent to look for correlations between the physical structure of the monomer mixture and copolymerization than in previously studied systems where polymerization was less than 20%. The system chosen on this basis and which is described in this paper comprises N-vinyl carbazole and N-phenylacrylamide.

Experimental

Purified samples of N-vinyl carbazole (NVC), m.pt. 68 °C and N-phenyl acrylamide (NPhA) ,m.pt. 107 °C were obtained by recrystallization of laboratory reagent chemicals.

Samples for differential thermal analysis (DTA) were prepared by heating for about 5 minutes at 10 °C above the melting point and leaving to cool in about one hour to room temperature. Samples were pulverized by shearing for 2 minutes in a Wig-L-Bug Dental Mill. DTA runs were made with samples (2 mg) heated from room temperature at 5 °C/min under nitrogen in a Perkin-Elmer differential scanning calorimeter (DSC-1).

Mixtures for polymerization studies were generally made up by repeated melting and degassing of the two monomers in pyrex tubes which were eventually sealed in vacuo. The monomers were then just melted and maintained as a melt for about 5 minutes before being left to cool to room temperature over a period of one-half to two hours. Samples were then immediately exposed to Co-60 γ-rays at constant temperature (± 1°C) at a dose rate of 0.2 Mrad/hr. Immediately after irradiation the tubes were opened to air and plunged into benzene to inhibit post-polymerization reactions.

The irradiated mixture was separated into four fractions as follows:

Solvent was evaporated from a benzene extract of the irradiated mixture. The residue was extracted with ethyl alcohol to yield Fraction I (soluble) and Fraction II (insoluble). As judged by melting point determinations, Fraction I consisted of unreacted monomers. Fraction II was found to be a polymeric product consisting mainly of NVC units although infra-red analysis usually revealed inclusion of a few per cent of NPhA. This fraction will subsequently be given the approximate designation " poly-NVC ".

The portion of the irradiated mixture insoluble in benzene proved difficult to separate and the following tedious steps appeared to be necessary. First, the insoluble portion was extracted with a mixture of benzene and acetone (80/20) and a precipitate obtained from the extract by addition of diethyl ether. This precipitate was subjected to a similar treatment but using benzene and acetone in the ratio of

20/80 to provide a second precipitate. Finally, the second precipitate was extracted with acetone and the insoluble portion designated as fraction III. Infra-red and oxygen analyses showed this fraction to consist of comparable amounts of NVC and NPhA and it will be designated as " copolymer ". The material recovered from these various extracts was bulked together (Fraction IV) and found to consist mainly of NPhA although always with a few per cent of NVC. This fraction will be designated, approximately, as " poly-NPhA ".

Differential thermogravimetric analyses (DTA) were made with a specially designed instrument. In every case the sample was heated at 5 °C/min in nitrogen from room temperature and weight and temperature recorded continuously.

RESULTS AND DISCUSSION

A phase diagram indicates that a eutectic with a melting point of 61°C is formed by a binary mixture containing 67% NVC, by weight (Fig. 4). γ-Irradiation of a mixture of similar composition, actually containing 65% NVC, at 55 °C results in virtually complete polymerization (> 95%) after a dose of several Mrad (Table 4a). The

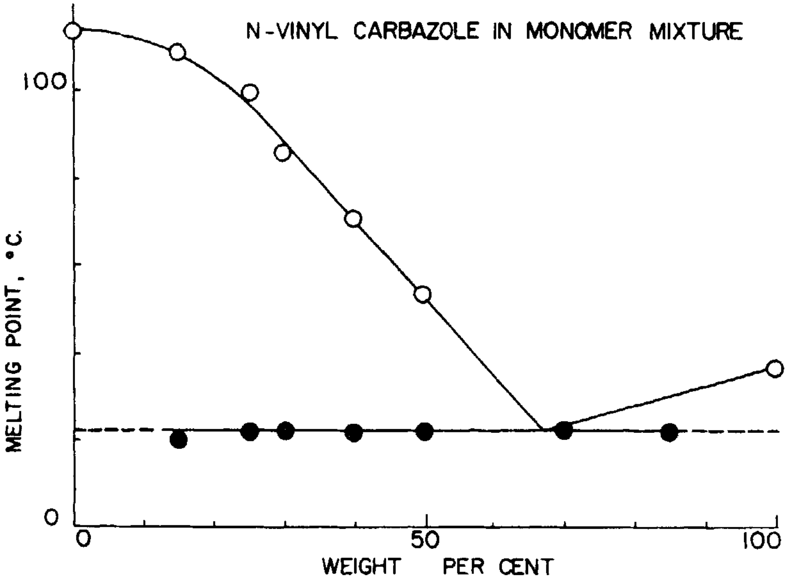

Figure 4. Phase diagram of the system N-vinyl carbazole/N-phenylacrylamide.

analytical data are somewhat erratic but indicate that about one-half of the monomer is converted into copolymer and the remainder into two " homopolymers ". Similar results were obtained with a monomer feed ratio of 50 : 50 but with indications of a lower maximum yield of copolymer (Table 4). This trend is made more obvious by varying the monomer feed ratio over a wider range and is consistent with a maximum yield of copolymer being obtained from the eutectic composition (Table 4c). Previously, a maximum rate of copolymerization has been reported to occur at the eutectic composition for a number of systems.[11,12,14] On the other hand the present observation that the proportion of NPhA in the copolymer varies according to its proportion in the monomer feed (see Table 4 footnote) is in contrast to previously studied systems in which copolymer composition approximated to the eutectic composition irrespective of the monomer feed ratio.[11,13]

TABLE 4 Influence of Dose and Monomer Feed on Polymerization at 55 °C

Monomer Feed	Dose	% Conversion of Monomer to Polymer		
(NVC : NPhA)	(Mrad)	poly-NVC	poly-NPhA	Copolymer
(a) 65 : 35	1.1	42	0	8
	2.2	28	6	57
	4.5	27	30	35
	8.4	26	13	54
(b) 50 : 50	1.2	38	14	48
	2.3	37	19	44
	4.1	lost	10	41
	8.1	12	42	47
(c) 90 : 10	4.8	61	8	22[1]
67 : 33	4.8	not recovered	not recovered	61[2]
40 : 60	4.8	20	22	12[3]
20 : 80	4.8	14	6	0
Sample number:	1	2	3	
% NPhA in copolymer:	16.0	26.0	31.5	

Careful examination of the irradiated samples listed in Table 4 showed no evidence of melting, for example no flow of sample during irradiation could be detected in a tilted tube. However, to minimize the further, seemingly imponderable, possibility of melting in localized zones further experiments were carried out at 43 °C i.e. at 18 °C below the melting point of the eutectic. At this stage in the experimental work it was suspected that one factor which should be better controlled to attain more reproducible results is the thermal history of the melt prior to irradiation. Therefore, varying thermal histories are noted in Table 5 although the only point to be made here is that these encompass within their range all the conditions appertaining to Table 4. The results obtained at 43 °C (Table 5) provide evidence that copolymerization really can occur in the solid state but, as would be expected from numerous investigations of solid state polymerization,[1] at a lower rate than just below the eutectic temperature (Table 4).

TABLE 5 Influence of Thermal History of Sample on Polymerization at 43 °C

Monomer feed (NVC : NPhA)	Thermal History	Dose (Mrad)	% Conversion of monomer to polymer poly-NVC	poly-NPhA	Copolymer
50 : 50	cooled from melt in ½ hour	4.0	6	1	6
65 : 35	cooled from melt in 3 hours	4.0	30	1	15
	cooled more gradually from melt	6.8	23	19	26
	in 3 hours	9.6	52	20	23

Some of the copolymers listed in Table 5 were studied by DTA in order to compare plots of weight loss versus temperature with those obtained from homopolymers, prepared by solid state irradiation of monomers, and also from made-up mixtures. Previously such comparisons have been made in order to differentiate between random and block copolymers. The weight loss plot for a random copolymer is generally found to be smooth and to lie between those of the two homopolymers. By contrast, a block copolymer shows an initial weight loss approximating the content of the more readily degraded component.[15,16] By reference to these criteria the present results provide evidence that the copolymer formed by irradiation approximates to a random rather than to a block copolymer (Fig. 5).

The results outlined above are in general agreement with previous reports that a copolymer may be prepared by irradiation of a solid

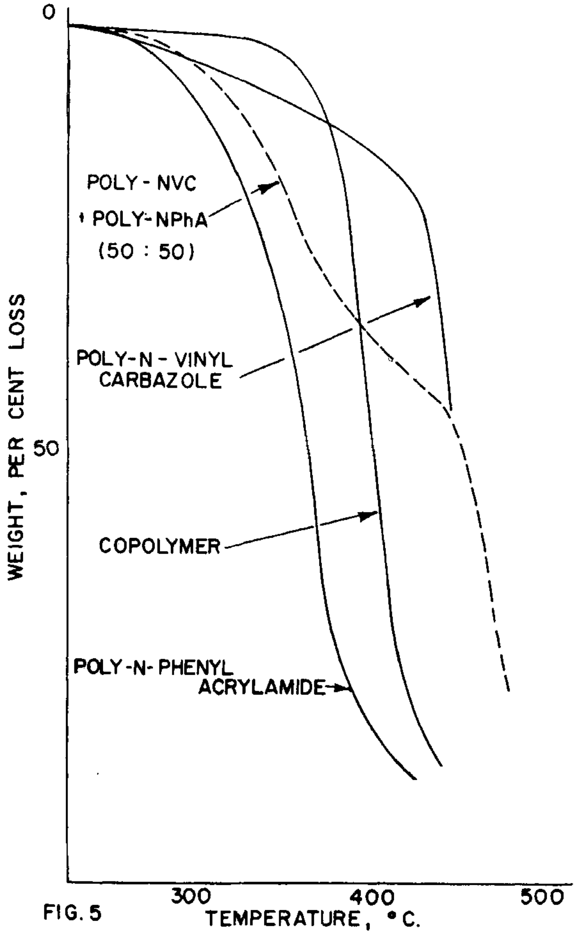

FIG. 5

Figure 5. Thermogravimetric analysis of various polymers. The copolymer comprised about 30% N-phenylacrylamide.

eutectic. Moreover, a high polymer is formed in which the monomer units are distributed more or less at random. The problem remains that it seems difficult to reconcile such an observation with the model of a solid organic eutectic as comprising separate crystals of each monomer. With this problem in mind the solidification of the eutectic melt and its subsequent ageing was observed carefully. At first a transparent rigid mass was formed but after a few hours at room temperature this began to appear increasingly opaque and to exhibit a light lavender coloration. After several days the coloration had faded and the sample appeared as a white crystalline mass. X-ray diffraction patterns revealed the presence of large well oriented crystals which were subsequently sought and found using an optical microscope (crystal diameters, 10–100μ).

The simplest explanation of the above observations is that the melt first forms a glass which, over a period of days, transforms to a polycrystalline mass. Previously, it has been reported that some eutectic mixtures which consist of a single monomer and an organic compound do form a glass and that the monomer can polymerize readily even when irradiated at a low temperature. Further it has been shown that glass formation is favored in cases where there is a strong interaction between the monomer and the other component of the eutectic.[17] Such interaction might favour passage of the system through the melting point without crystallization occurring for a variety of reasons (cf. ref. 18). In the present system evidence of interaction between the two monomers may be inferred from the observed coloration which may be presumed to fade as the two monomers are segregated during crystallization.

Most strikingly even after a dose of 10 Mrad, at 43 °C, a sample of eutectic composition which had aged for 72 hours and formed large crystals gave, virtually only a mixture of homopolymers, viz. 40% poly-NVC, 20% poly-NPhA, and 2% copolymer. Hence, in a single system it is possible to get, on the one hand, a higher yield of copolymer than ever attained before from a solid eutectic and, on the other, a mixture of homopolymers such as has been reported previously to result from irradiation of a number of systems.[1] It remains to check whether polymerization in glassy regions is the important factor in accounting for copolymerization in other eutectics.

Acknowledgments

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