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Solvent Effect in Radical Copolymerisation of N-vinylcarbazole and Methylmethacrylate

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Summary

Radical copolymerisation of MMA(r_1) and NVC(r_2) yields values of the apparent reactivity ratios r_1 = 1.80, r_2 = 0.06 (benzene) and r_1 = 0.57, r_2 = 0.75 (methanol) at 55°C. It is suggested that the apparent increase in reactivity of NVC in methanol arises from high local monomer concentrations due to formation of microphases containing the growing copolymer chains in which NVC is preferentially partitioned. Fluorescence emission and u.v. absorption spectra for copolymers prepared in both solvents are identical and consistent with the occurrence of only very short sequences of NVC units.

Introduction

N-vinylcarbazole (NVC) is a strong electron donor molecule which polymerises readily by cationic and free radical chain processes. It has proved of particular value in stimulating research into initiation of polymerisation via charge transfer interactions (HYDE and LEDWITH, 1974) and its homopolymer, similarly, has the electron donor properties typical of many organic photoconductors (PENWELL et al, 1978); (PEARSON et al, 1979). Another interesting feature of polymers derived from NVC is the complex luminescence behaviour (JOHNSON, 1975), studies of which are greatly facilitated by the characteristic u.v. absorption of carbazole derivatives in the 300-350 nm region. More recently we have shown (CHIELLINI et al, 1978) that the same light absorption characteristics make carbazole substituents convenient probes for studies of circular dichroism of optically active polymers. In particular, optically active co-polymers derived from NVC and optically active monomers such as (-)menthylvinylether exhibit circular dichroism indicative of the monomer composition and sequence distribution.

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As part of these studies it has become necessary to have a better understanding of the copolymerisation reactivity of NVC with common polymerisable monomers such as acrylates and methacrylates. Previously we have observed (HYDE and LEDWITH, 1974; CRELLIN and LEDWITH, 1975), from preliminary studies, that NVC and methyl methacrylate (MMA) appear to give different copolymers when polymerised in different solvents and, in the present paper, copolymerisation behaviour in methanol and benzene is reported in detail.

Experimental

NVC (Polysciences) was recrystallised three times from methanol. MMA (B.D.H) was washed free from inhibitor and distilled immediately before use. Polymerisations were carried out with initiation by AIBN at 55°C in sealed tubes after the usual outgassing procedure and were terminated by pouring reaction mixtures into methanol. The copolymers were isolated by filtration and purified by repeated precipitations from dichloromethane into methanol; copolymer structures were characterised by i.r., u.v., and n.m.r. spectroscopy. Copolymer compositions were analysed by quantitative u.v. analysis of dichloromethane solutions assuming a composition independent absorption at 342 nm with an extinction coefficient of $3.61 \times 10^3 M^{-1}cm^{-1}$. Unresolved ^1H n.m.r. spectra taken in $CDCl_3$ at room temperature gave intensity ratios for aromatic (carbazole) and aliphatic protons in excellent agreement with the u.v. data. Fluorescence emission spectra were recorded in outgassed solutions on a Perkin-Elmer MPF-43 spectrofluorimeter.

Results and Discussion

Copolymerisation of NVC and MMA at 55°C in benzene, methanol, acetone, isopropanol and n-pentane solvents is described by the data of Table 1. The concentration range employed for methanol solutions is somewhat restricted because of the limited solubility of NVC. Evaluation of monomer reactivities by the Fineman-Ross method gave the following results:

Benzene: $r_1(MMA) = 1.80$, $r_2(NVC) = 0.06$

Methanol: $r_1(MMA) = 0.57$, $r_2(NVC) = 0.75$

which, for benzene solutions are in reasonable agreement with literature values (75°C) $r_1(MMA) = 2.0$ and $r_2(NVC) = 0.04$ (HART, 1961) and (60°C), $r_1(MMA) = 1.64$ $r_2(NVC) = 0.15$ (BEVINGTON et al, 1979). There are no previous literature results for polymerisations in methanol.

TABLE 1

Copolymerisation of NVC and MMA at 55°C

Run No.	Solvent	M_1	m_1	F	f
1	benzene (2.3)[a]	91.45	95.34	10.69	20.46
2	"	82.88	89.79	4.84	8.79
3	"	74.34	85.72	2.89	6.00
4	"	65.69	84.44	1.91	5.43
5	"	48.47	71.47	0.94	2.51
6	"	35.68	65.95	0.55	1.94
7	"	30.28	58.19	0.43	1.39
8	"	15.84	43.06	0.19	0.76
9	methanol (32.6)[a]	90.91	86.14	10.00	6.21
10	"	88.24	84.34	7.50	5.38
11	"	83.23	75.88	4.96	3.15
12	"	71.43	58.51	2.50	1.41
13	"	50.29	45.35	1.07	0.83
14	"	43.16	46.37	0.76	0.86
15	"	16.79	36.79	0.20	0.58
16	acetone (20.7)[a]	90.00	93.67	9.00	14.80
17	"	83.23	89.01	4.96	8.09
18	"	75.00	86.09	3.00	6.19
19	isopropanol(18.3)[a]	83.23	78.63	4.96	3.68
20	n-pentane (1.8)[a]	83.23	85.50	4.96	5.89

a. Dielectric constant (20-25°C).

For all experiments the initial total concentrations of comonomers was in the range 0.47 - 1.73M, reaction times were from 20-40 minutes at 55°C and conversions were limited to 4-5% except for runs 7,8 for which conversions reached 7.4 and 9.8% respectively. The initial initiator was AIBN and, for each polymerisation, [Comonomers]/[AIBN] = 50.

M_1 = mol % MMA in feed mixture $F = \frac{M_1}{M_2}$; $f = \frac{m_1}{m_2}$

m_1 = mol % MMA in copolymer

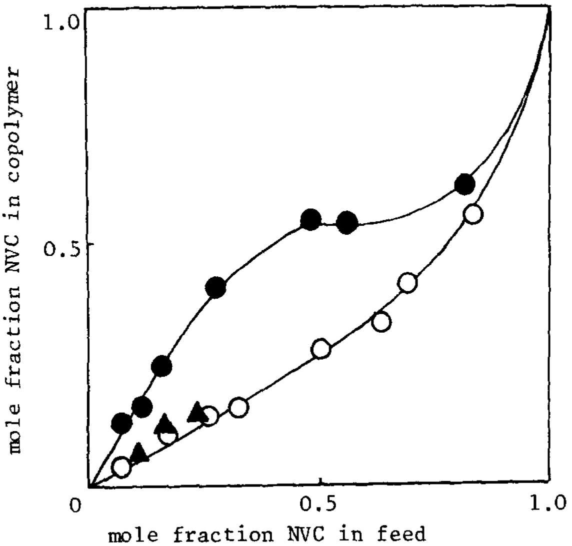

Figure 1 - Monomer feed - Composition Curves for copolymerisation of MMA and NVC in different solvents at 55°C.

O benzene O methanol Δ acetone

The very significant difference in reactivity ratios for common monomers in benzene and methanol solvents is surprising and requires comment. Although homopolymers of NVC and MMA and copolymers NVC-MMA are largely insoluble in pure methanol at room temperature, precipitation was observed only towards the end of the polymerisations in methanol containing MMA monomer at 55°C. It seems unlikely, therefore, that the large increase in reactivity of NVC in methanol (compared with benzene) arises from any solid polymer precipitation problems. On the other hand, it is probably that the growing copolymer chains, which are completely soluble in benzene, might form "microphases" in the precipitant methanol before the onset of polymer precipitation. This would afford the possibility for a partitioning of monomers between the growing copolymer microphase and the bulk solvent phase. Significantly, the solubility of NVC in methanol is low ($\sim$ 0.12M at 25°C) and hence it is entirely reasonable to expect that NVC would preferentially associate with the growing copolymer microphase than with bulk methanol. Overall this would result in an apparent increase in free radical polymerisability for NVC in methanol, as observed experimentally. Very similar behaviour has been reported recently for copolymerisation of styrene and methacrylic acid in various solvents. In this case analysis of the product copolymers by 300 MHz ^{1}H n.m.r spectroscopy showed clearly that the monomer sequence distributions were not influenced by solvent effects on apparent reactivities (PLOCHOCKA and HARWOOD, 1978).

TABLE 2

Apparent Sequence Distributions for Copolymers of MMA and NVC

Run No.[a]	f[a]	$\bar{\ell}_2$[b]	$W_{2(n)}$[c]				$X_{2(n)}$[d]			
			1	2	3	4	1	2	3	4
4	5.43	1.03	97.0	2.9	0.1	0.0	94.1	5.6	0.3	0.0
8	0.76	1.32	75.8	18.2	4.4	1.0	57.4	27.6	9.9	3.2
10	5.38	1.10	90.9	8.3	0.7	0.7	82.6	15.1	1.9	0.4
15	0.58	4.71	21.2	16.7	13.2	10.4	4.5	7.1	8.4	8.8

a) Data from Table 1 (run Nos. 4,8 in benzene and 10,15 in methanol solvents). b) Mean sequence length of NVC units. c) Probability for closed sequences of n units of NVC. d) Mole fraction (%) of corresponding units involved in the formation of a general sequence of n units of NVC.

An alternative explanation might be that the increased polarity of methanol compared with benzene is in some way responsible for the higher reactivity of NVC. However, as shown in Table 1, (Run nos. 2,11,17 and 19) acetone which is a solvent for the copolymers gives reactivities similar to those in benzene whilst isopropanol, which is a precipitant for the copolymers, gives results similar to those obtained in methanol. Whilst the polarities of benzene and acetone are very different, the two solvents exert a similar effect on copolymerisation of NVC and MMA (Run nos. 2 and 17); the contrast with methanol is clearly indicated by the monomer feed - copolymer composition curves in Figure 1. Although n-pentane is a precipitant for the copolymers it is a much better solvent (x5) for NVC at room temperature than methanol or isopropanol and, as expected, gives copolymer with compositions (Run no.22) intermediate between those obtained in methanol and benzene.

Further support for microphase separation in pure methanol is provided by data for copolymerisations in mixed methanol-benzene solvents. Thus at constant monomer feed (M_1 = 83.23) identical polymerisations gave the following results (methanol/benzene volume ratio, copolymer composition m_1): 50/50, 87.50; 70/30, 85.11; 90/10, 84.07; 100/0, 75.88. The most significant change in copolymer composition takes place as the solvent mixture approaches pure methanol.

Reactivity ratios for NVC and MMA in benzene indicate a tendency to alternating copolymerisation (r_1r_2 = 0.11) which implies only very short sequences of NVC units even in copolymers having high carbazole content. Sequence distributions calculated for typical copolymers prepared in benzene are shown in Table 2.

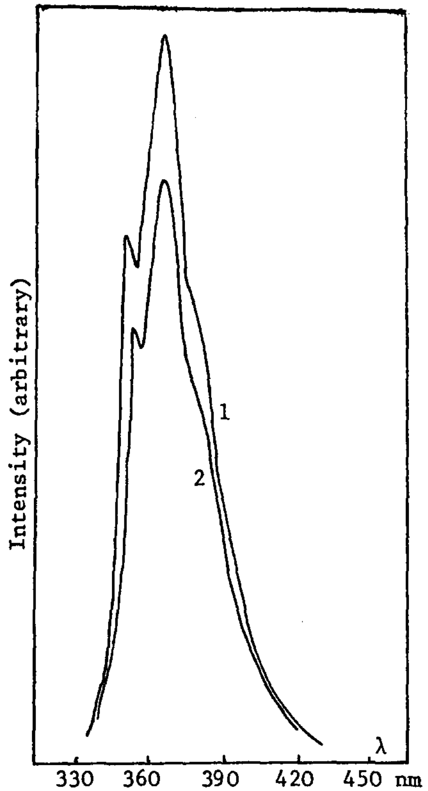

Figure 2 - Fluorescence spectra of MMA-NVC copolymers in CH_2Cl_2 at 25°C. (10^{-4} base mol NVC, excitation wavelength 330 nm). 1. 56.94 mol % NVC (prepared in benzene). 2. 57.46 mol % NVC (prepared in methanol.

Fluorescence emission spectra of samples of poly-(N-vinylcarbazole) indicate significant energy migration amongst the carbazole units with ultimate population of excimer traps. Formation of emitting excimers is directly influenced by the availability of long sequences of NVC units (HOUBEN et al, 1978). It would be expected therefore, that copolymers of NVC and MMA having only short NVC-sequences should not exhibit excimer formation as observed experimentally (Figure 2). Over a wide range of copolymer compositions, copolymers of NVC and MMA prepared in both benzene and methanol solvents give fluorescence emission spectra identical to that shown in Figure 2, characteristic of emission from isolated carbazole units, and suggesting that copolymers obtained in methanol solvent have only very short sequences of NVC units. On the other hand, values of the apparent reactivity ratios in methanol (r_1r_2 = 0.43) would suggest considerably longer sequences (Table 2) of NVC units than for corresponding copolymers obtained in benzene.

Figure 3 - U.V. absorption spectra of MMA-NVC copolymers in dioxan at 25°C. 1. 15.66 mol % NVC (prepared in benzene). 2. 56.94 mol % NVC (prepared in benzene). 3. 57.46 mol % NVC (prepared in methanol).

Additional evidence for the short length of NVC sequences in these copolymers is provided by their ultra-violet absorption spectra. It is already well established (CHERNOBAI et al, 1965) that whereas homopolymers of NVC give rise to a single absorption band at 230 nm in dioxane solvent, copolymers with rather low carbazole content exhibit two bands at 230 and 237 nm. The absorption at 237 nm is predominant in carbazole and its N-alkyl derivatives and may be taken to represent relatively isolated carbazole units in copolymers. Absorption spectra of copolymers prepared in the present work (Figure 3) are entirely consistent with this interpretation in so far as those with low carbazole content exhibit the most intense absorption at 237 nm and copolymers with more than 50% NVC content show strong evidence of relatively isolated carbazole units. Furthermore, as shown in Figure 3, copolymers prepared in benzene and methanol solvents and having similar compositions, give virtually identical absorption spectra. These results are readily understood if the growing polymer chains in methanol solvent are contained in microphases in which NVC is preferentially partitioned and hence, despite apparently different values of reactivity ratios, actual sequence distributions for polymers prepared in methanol and benzene are essentially equivalent.

Conclusions

Copolymerisation of NVC and MMA in benzene and methanol solvents yields very different values of reactivity ratios indicating that the reactivity of NVC appears to increase significantly and that of MMA decreases in methanol. However, fluorescence emission spectra of the copolymers are identical and show predominant monomeric carbazole emission. This result implies that copolymers from both solvents have only very short sequences of NVC units, and is strongly supported by u.v. absorption spectra in the 230-240 nm region. It is suggested that the apparent increase in reactivity of NVC in methanol arises from high local concentrations due to formation of microphases containing growing polymer chains in which NVC is preferentially partitioned.

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