Photopolymerization of *N*-vinylcarbazole in dichloromethane in the presence and absence of free radical photoinitiators

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The photopolymerization of *N*-vinylcarbazole in dichloromethane was investigated, both in the presence and absence of free radical photoinitiators. The steric microstructure of the poly(*N*-vinylcarbazole) (PVK) samples produced was monitored as a function of temperature qualitatively, using ^{1}H n.m.r. and quantitatively, using glass transition temperature measurements. The activation enthalpy and entropy differences between isotactic propagation when the previous diad was syndiotactic and syndiotactic propagation when the previous diad was isotactic $(\Delta H^{\ddagger}_{s/i} - \Delta H^{\ddagger}_{i/s})$ and $(\Delta S^{\ddagger}_{s/i} - \Delta S^{\ddagger}_{i/s})$ respectively were obtained from plots of log X_i/X_s *versus* $1/T$ for the free radically and cationically polymerized components of the PVK samples. Values for $(\Delta H^{\ddagger}_{s/i} - \Delta H^{\ddagger}_{i/s})$ and $(\Delta S^{\ddagger}_{s/i} - \Delta S^{\ddagger}_{i/s})$ of -2.65 kJ mol^{-1} and -11.7 J mol^{-1} grad^{-1} respectively were found for free radically polymerized fractions and $+260$ J mol^{-1} and -0.3 J mol^{-1} grad^{-1} for cationically polymerized fractions.

Keywords Free radical polymerization; cationic polymerization; photopolymerization; *N*-vinylcarbazole; stereocontrol

INTRODUCTION

N-vinylcarbazole (VK) has been reported[1,2] to undergo rapid cationic polymerization when VK solutions in dichloromethane at +10° to +20°C are irradiated with u.v. light. Moreover, Tada *et al.*[1] have shown by the addition of free radical [1,1 diphenyl-2-picrylhydazyl (DPPH)] or cationic [*N*,*N*-dimethylformamide (DMF)] polymerization inhibitors that, in the absence of oxygen, *ca.* 75% of the poly(*N*-vinylcarbazole) (PVK) produced was cationically polymerized and *ca.* 25% free radically polymerized. They also observed the presence of a transient absorption which was assignable to the VK radical cation, when VK was irradiated with u.v. light in a similar solvent (1,2 dichloroethane). These observations were interpreted by suggesting that the VK triplet was responsible for initiating the free radical polymerization observed and the VK cation radical for initiating the cationic polymerization.

The present paper shows that simultaneous but independent free radical and cationic polymerizations are observed upon u.v. irradiation of VK in dichloromethane over a large range of temperatures, both in the presence and in the absence of free radical photoinitiators. Moreover, an investigation of the steric microstructure of the free radically and cationically polymerized components, as a function of temperature, reveals that the steric microstructure of the cationic components is almost independent of the polymerization temperature, whereas the free radical component exhibits a strongly polymerization temperature-dependent steric microstructure.

EXPERIMENTAL

The *N*-vinylcarbazole (VK) was obtained from Fluka and was purified by vacuum distillation at *ca.* 110°C and then stored under nitrogen. The VK solutions were made up and used under dry nitrogen. The dichloromethane and *N*,*N*-dimethylformamide used were p.a. grade (Merck) and were dried over a molecular sieve before use. The free radical initiators used were α,α′-azobisisobutyronitrile (AIBN) and benzoin methyl ether (BME) and there were obtained from Merck. The AIBN was recrystallized from methanol before use and BME was used directly without further purification.

The photopolymerizations were carried out in a Mangel reactor in which the Philips HPK 125W/L lamp is positioned centrally with respect to the solution being irradiated. Temperature control was achieved using a thermostatically controlled water bath, a Haake KT52 cryostatt and a regulated liquid nitrogen-heater system in the temperature ranges 25° to 40°C, 25° to −42°C and −42° to −120°C respectively. At completion of the polymerizations, the PVK samples were precipitated by addition to methanol accompanied by rapid stirring. After twofold reprecipitation by the dropwise addition of benzene solutions to hot methanol to remove any unreacted monomer, the PVK samples were fractionated by the dropwise addition of methanol to a 1.1 wt% solution of PVK in benzene at 22°C. Each fraction was then reprecipitated under the same conditions, i.e., benzene to methanol ratio, to ensure fractions with very narrow molecular weight distributions were obtained. The molecular weights of these fractions were estimated from the dependence of M_n upon the volume ratio of benzene to methanol shown in *Figure 1*. This was constructed using the molecular weight distribution data

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obtained for very narrow molecular weight distribution fractions of free radically polymerized PVK samples.

The polymerization conditions for PVK samples photopolymerized in the presence and in the absence of a free radical photoinitiator together with the yields obtained are given in *Table 1*. In general, with the exception of runs UV 85 and UV 86, the yields obtained were quite reproducible. The reason for the apparent irreproducibility in these two exceptional cases is unknown, but may have been due to a difference in the light intensity.

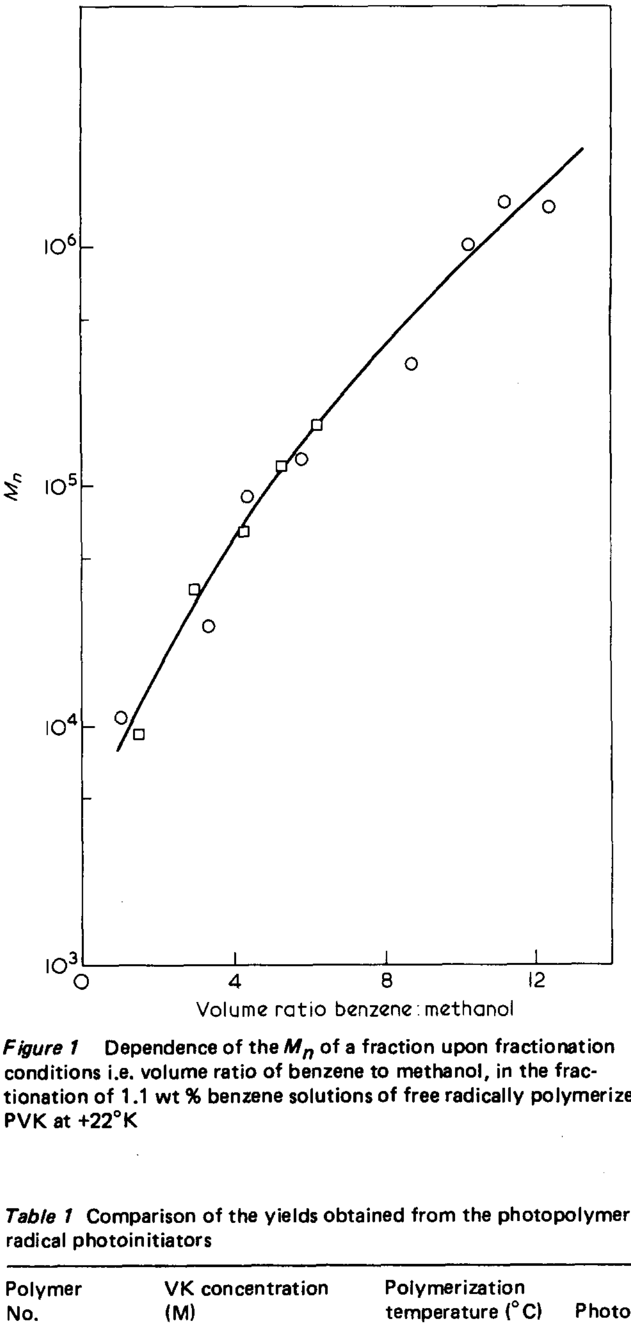

Figure 1 **Dependence of the M_n of a fraction upon fractionation conditions i.e. volume ratio of benzene to methanol, in the fractionation of 1.1 wt % benzene solutions of free radically polymerized PVK at +22°K**

The molecular weight distributions of the PVK samples obtained by photopolymerization in dichloromethane were determined using a hybrid g.p.c. system consisting of a Waters pump and a Pye Unicam LC3 u.v. detector with the following combination of microstyrogel columns: 10^6 Å, 10^5 Å, 10^4 Å, 10^3 Å and 500 Å. These measurements were carried out at room temperature using tetrahydrofuran solutions and Benoit corrections[3] were applied to convert the polystyrene calibration curve into a PVK calibration curve, using the data of Boni *et al.*[4] and Sitaramaiah *et al.*[5].

The fractionated and unfractionated PVK samples were characterized by ^{1}H n.m.r. and glass transition temperature, T_g, measurements. The ^{1}H n.m.r. measurements were carried out using a Varian L-100-12 FT spectrometer and on solutions of PVK in tetradeutero-1,2-dibromomethane (Merck) at +120°C. Unlike a previous study on free radically polymerized PVK samples[6], the tacticity values derived from the two methine peak heights of the ^{1}H n.m.r. spectra, assuming that the high frequency and low frequency peak heights represent the syndiotactic and isotactic mole fractions respectively, yield isotactic mole fractions, X_i, which were *ca.* 20% too low when compared with X_i values derived from glass transition temperature measurements. This may be due to the methine spectrum being an incompletely resolved triad spectrum with a large X_{is} peak or to the diad peaks having distorted peak shapes, making the peak heights unrepresentative of the peak areas. Glass transition temperature measurements were carried out as described previously[7,8] using a Perkin Elmer DSC 1 B differential scanning calorimeter. Only the fractionated samples were investigated and these were dried at 120°–150°C overnight in a rotary pump vacuum. The glass transition temperatures used for the calculation of X_i and X_s were molecular weight independent T_g's[7]. Where necessary a correction was applied to the measured T_g's, taking into account the estimated molecular weight of the fraction and the molecular weight dependence of the T_g of PVK[7].

Table 1 Comparison of the yields obtained from the photopolymerization of VK in dichloromethane in the presence and absence of free radical photoinitiators

Polymer No.	VK concentration (M)	Polymerization temperature (°C)	Photoinitiator	Photoinitiator conc (M)	Polymerization time (h)	Polymerization yield (%)
UV46	0.20	+15	AIBN	3.66×10^{-3}	2	72.5
UV47	0.20	+15	BME	2.66×10^{-3}	2	46.6
UV48	0.20	+15	AIBN	3.66×10^{-3}	2	82.0
UV60	0.16	+40	BME	2.66×10^{-3}	2	77.0
UV87	0.20	+25	–	–	4.26	36.0
UV88	0.20	+26	–	–	4.62	31.0
UV49	0.20	–5	AIBN	3.66×10^{-3}	2	82.0
UV53	0.20	–5	BME	2.66×10^{-3}	2	85.5
UV85	0.20	–3	–	–	3.63	58.5
UV86	0.20	–3	–	–	5.41	26.4
UV55	0.12	–25	AIBN	6.71×10^{-3}	3	40.3
UV56	0.20	–25	BME	2.66×10^{-3}	4	49.2
UV84	0.20	–20.5	–	–	6.68	77.2

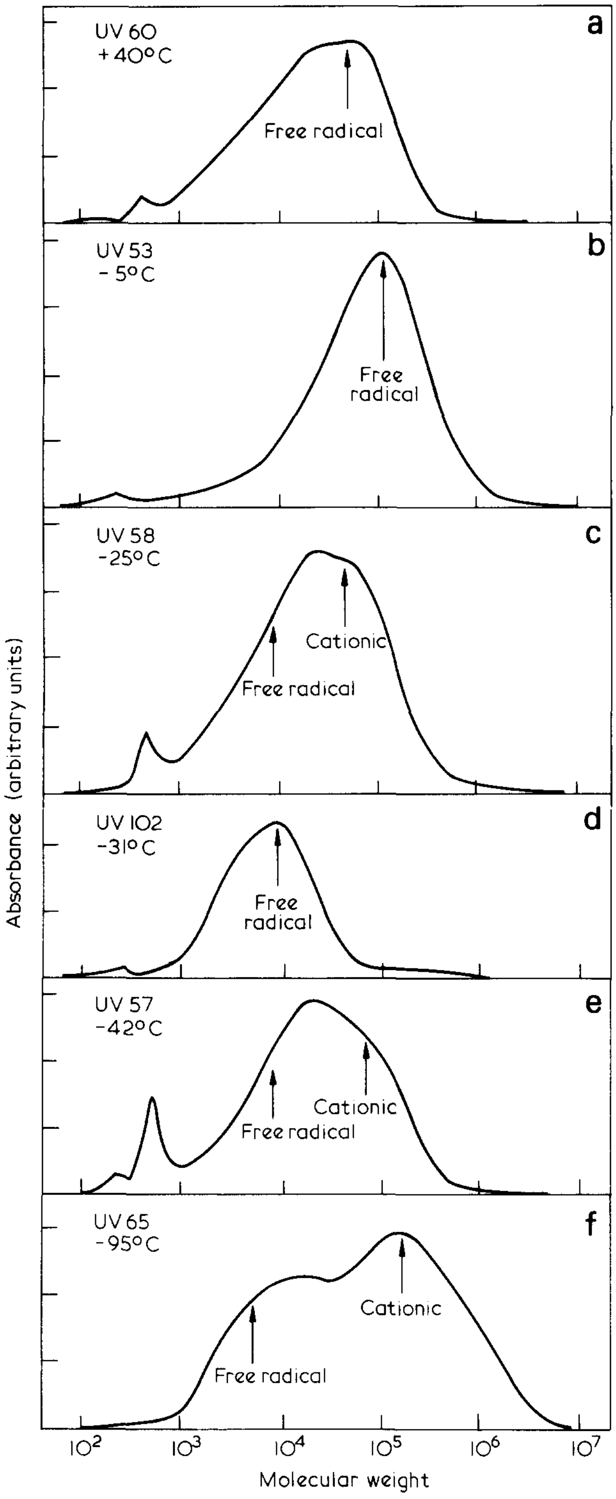

Figure 2 Molecular weight distributions of PVK samples photopolymerized in dichloromethane in the presence of free radical photoinitiators at different temperatures: (a) +40°C; (b) −5°C; (c) −25°C; (d) −31°C (in presence of DMF); (e) −42°C and (f) −95°C

RESULTS

In general the presence of one or more polymerization processes can be established by the molecular weight distribution (*MWD*) of the polymer being unimodal or polymodal. A broad *MWD* may also indicate polymodality or may simply be due to the increased *MWD* broadening observed with increasing polymerization temperature, in particular above room temperature. The *MWD*'s for several PVK samples photopolymerized at different temperatures in the presence and in the absence of the free radical photoinitiator BME are shown in *Figures 2* and *3* respectively.

The assignment of the components of the *MWD*'s shown in these figures is aided by the observation of Tada *et al.*[1] that the major and minor components of PVK photopolymerized at room temperature in dichloromethane in the absence of free radical initiators, were respectively cationic and free radical in origin. Thus by analogy the high molecular weight shoulder and the low molecular weight peak in *Figure 3a* can be assigned to free radically and cationically polymerized PVK respectively. The *MWD* of free radically photopolymerized PVK will be determined solely by the polymerization temperature and the activation energies of propagation and termination and therefore the presence or absence of photoinitiator will not affect the *MWD* (see Discussion). This fact was used to compare the *MWD*'s of the cationically polymerized component of samples prepared by photopolymerization of VK in dichloromethane in the presence and absence of BME. A control experiment was carried out in which the cationic polymerization inhibitor *N*,*N*-dimethyl formamide (DMF) was added. A comparison of the *MWD*'s of PVK prepared in the presence of BME and DMF at −31°C (*Figure 2d*) with those of PVK prepared at −42°C in the presence of BME (*Figure 2e*) and at −36°C in the absence

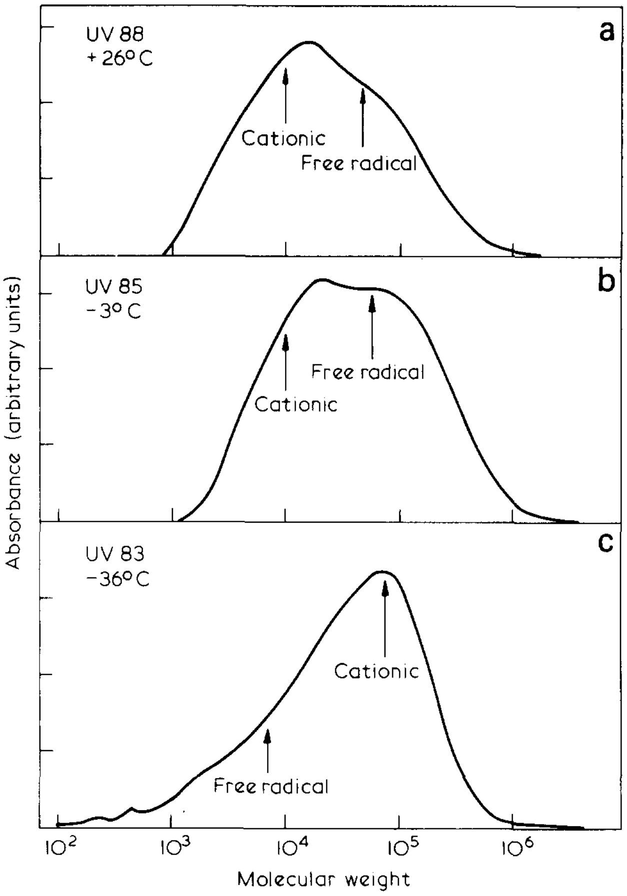

Figure 3 Molecular weight distributions of PVK samples photopolymerized in dichloromethane in the absence of free radical photoinitiators at different temperatures: (a) +26°C; (b) −3°C; and (c) −36°C

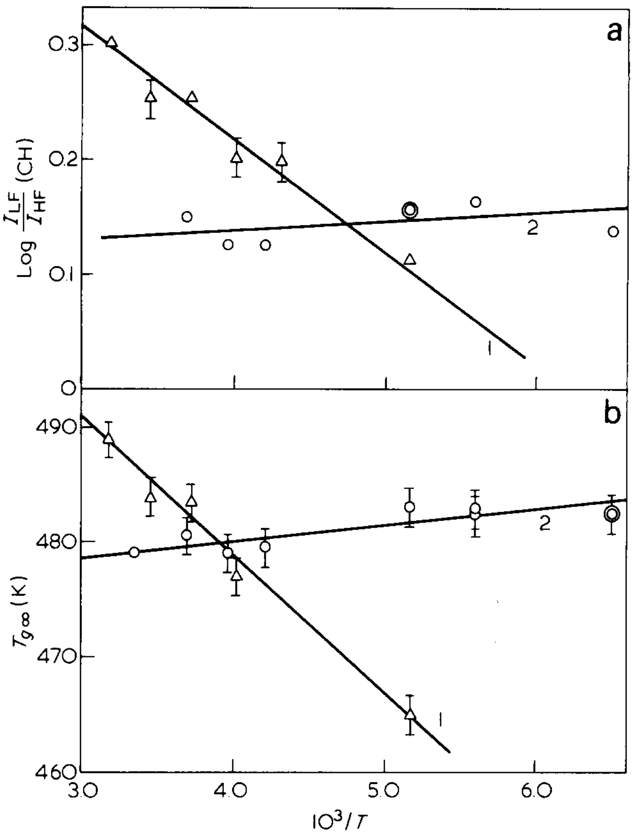

Figure 4 Dependences of (a) log I_{LF}/I_{HF} (CH); and (b) $T_{g\infty}$ upon $1/T$ for: (1) the free radically polymerized component and (2) the cationically polymerized component

of BME (*Figure 3c*) shows that the free radically polymerized component increases relative to the cationically polymerized component upon addition of BME and that the high molecular weight cationically polymerized components have similar *MWD*'s. This indicates that the propagation and termination processes in the photoinitiated cationic polymerization of VK in the presence and in the absence of BME were similar and therefore that the counterions and hence the initiation processes were identical. This knowledge can now be used to examine the temperature dependencies of the molecular weights of the free radically and cationally polymerized components.

The free radically polymerized components of photopolymerized PVK samples exhibited a decrease in molecular weight with decreasing polymerization temperature (see *Figures 2* and *3*). Alternatively the cationically polymerized components of PVK samples exhibited an increase in molecular weight with decreasing polymerization temperature (see *Figures 2* and *3*). In addition, in the temperature range +40° to −30°C, the rate of the predominantly free radical photopolymerization observed in the presence of BME or AIBN decreased with decreasing polymerization temperature, whereas in the same temperature range the rate of the predominantly cationic photopolymerization observed in their absence increased with decreasing temperature (see *Table 1*).

Further evidence for the entirely separate nature of the simultaneous free radical and cationic polymerization can be obtained from the steric microstructures of the respective components and their polymerization temperature dependencies. ^{1}H n.m.r.[6] and glass transition temperature (T_g) measurements[7] have been used to investigate the steric microstructures of narrow *MWD* fractions corresponding to the free radically and cationically polymerized components. Variations in the peak height ratio of the high frequency (HF) and low frequency (LF) peaks corresponding to the methine group have been used as a qualitative yardstick for steric microstructure changes. In *Figure 4a* the logarithm of this peak height ratio is plotted as a function of reciprocal temperature for fractions corresponding to the respective components. It is apparent that the free radically polymerized fractions (line 1) exhibit a very strong dependence of steric microstructure upon polymerization temperature, whereas the cationically polymerized fractions (line 2) exhibit a very weak dependence of steric microstructure upon polymerization temperature. This is further evidence for the separate nature of the free radical and cationic polymerization processes.

Quantitative information about the steric microstructure of the free radically and cationically polymerized components was obtained from T_g temperature measurements. In *Figure 4b* the molecular weight independent glass transition temperature, $T_{g\infty}$, is plotted against reciprocal temperature for the free radically and cationically polymerized fractions. Comparison of *Figures 4a* and *4b* shows a clear correlation between $T_{g\infty}$ and steric microstructure. This dependence can be described by the relationship[7]:

$$(T_{g\infty}-399)(1-X_s)+(T_{g\infty}-549)X_s=0 \qquad (1)$$

where X_s and $X_i(=(1-X_s))$ are the syndiotactic and isotactic diad mole fractions respectively.

The X_s values for the free radically and cationically polymerized fractions were calculated using equation (1) and are shown in *Tables 2* and *3* respectively. In *Figure 5* the data in *Tables 2* and *3* have been plotted in the form of log X_i/X_s *versus* T^{-1} for the free radically (continuous line) and cationically (broken line) polymerized fractions respectively. These plots yield the enthalpy and entropy differences between isotactic and syndiotactic propagation, as shown in equation (2)[9]:

$$\frac{X_i}{X_s}=\exp\frac{(\Delta S^{\ddagger}_{s/i}-\Delta S^{\ddagger}_{i/s})}{R}\exp\left[\frac{(-\Delta H^{\ddagger}_{s/i}-\Delta H^{\ddagger}_{i/s})}{RT}\right] \qquad (2)$$

where R is the gas constant and the terms $(\Delta S^{\ddagger}_{s/i}-\Delta S^{\ddagger}_{i/s})$ and $(\Delta H^{\ddagger}_{s/i}-\Delta H^{\ddagger}_{i/s})$ represent the activation entropy and enthalpy differences between isotactic propagation when the previous unit was syndiotactic and syndiotactic propagation when the previous unit was isotactic. The

Table 2 Polymerization conditions and steric microstructures of the free radically polymerized component

Polymer No.	VK concentration (M)	Polymerization temperature (°C)	Photoinitiator	Diad mole fraction X_i	Diad mole fraction X_s
UV59	0.20	−80	BME	0.56	0.44
UV58	0.20	−25	BME	0.48	0.52
UV53	0.20	−5	BME	0.43^5	0.56^5
UV48	0.20	+15	AIBN	0.43^5	0.56^5
UV60	0.16	+40	BME	0.40	0.60

Table 3 Polymerization conditions and steric microstructures of the cationically polymerized component

Polymer No.	VK concentration (M)	Polymerization temperature (°C)	Photoinitiator	Diad mole fraction	
				X_i	X_s
UV66	0.20	−120	BME	0.44^5	0.55^5
UV65	0.17	−95	BME	0.44^5	0.55^5
UV59	0.20	−80	BME	0.44	0.56
UV83	0.20	−36	–	0.46^5	0.53^5
UV84	0.20	−20.5	–	0.46^5	0.53^5
UV86	0.20	−3	–	0.45^5	0.54^5
UV87	0.20	+25	–	0.46^5	0.53^5

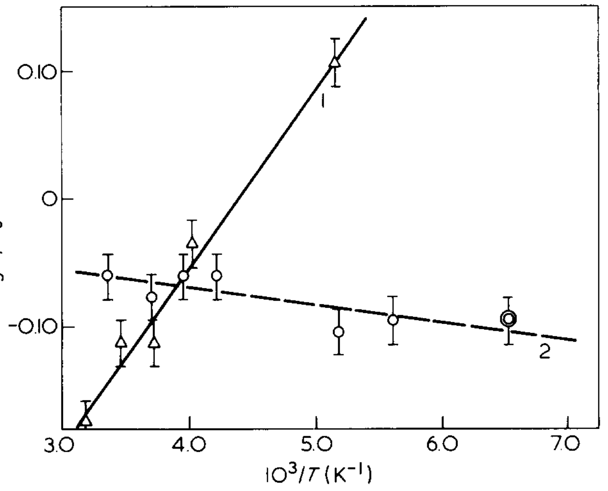

Figure 5 Dependence of log X_i/X_s upon $1/T$ for: (1) the free radically polymerized component and (2) the cationically polymerized component

plots in *Figure 5* yield $(\Delta S^{\ddagger}_{s/i} - \Delta S^{\ddagger}_{i/s})$ and $(\Delta H^{\ddagger}_{s/i} - \Delta H^{\ddagger}_{i/s})$ values for free radically polymerized fractions of -11.7 ± 0.4 J mol^{-1} grad^{-1} and -2.65 ± 0.1 kJ mol^{-1} and for cationically polymerized fractions values of -0.3 ± 0.1 J mol^{-1} grad^{-1} and 260 ± 50 J mol^{-1} respectively.

DISCUSSION

U.v. excitation of VK in dichloromethane in the absence of BME or AIBN induced both free radical and cationic polymerization. These appear to be completely separate processes as shown by the observation of bimodal *MWD*'s and the separation of the free radically and cationically polymerized components *via* fractional precipitation. The polymerization dependences of the molecular weight of the free radical and cationic components and hence the relative yields, since the number of active centres will solely depend upon the irradiation conditions, can be explained in terms of the kinetics of the polymerization processes. The temperature dependence of the degree of polymerization for free radical photopolymerization is given by[10]:

$$\frac{\mathrm{d}\ln \bar{x}_n}{\mathrm{d}\left(\frac{1}{T}\right)} = -\left(\frac{E_p - E_{t/2}}{R}\right) \tag{3}$$

where $\bar{x}_n$ is the average degree of polymerization and E_p and E_t are the propagation and termination activation energies respectively. Since $(E_p - E_{t/2})$ is always positive for free radical polymerization, the molecular weight will decrease with decreasing temperature as was observed for the free radically polymerized component. Indeed the dependence of peak molecular weight in the *MWD*'s upon polymerization temperature is fully consistent with Hughes *et al.*'s[11] data for the free radical polymerization of VK in THF.

For cationic polymerization, the temperature dependence of the degree of polymerization is given by[12]:

$$\frac{\mathrm{d}\ln \bar{x}_n}{\mathrm{d}\left(\frac{1}{T}\right)} = -\left(\frac{E_p - E_t}{R}\right)$$

and since $(E_p - E_t)$ is always negative, the molecular weight will decrease with increasing polymerization temperature, as was observed for the cationically polymerized component.

The polymerization temperature dependencies of the steric microstructure for the free radically and cationically polymerized components are strikingly different (see *Figure 5*). The large negative activation enthalpy difference, $(\Delta H^{\ddagger}_{s/i} - \Delta H^{\ddagger}_{i/s})$, observed for the free radically polymerized component, was consistent with $(\Delta H^{\ddagger}_{s/i} - \Delta H^{\ddagger}_{i/s})$ data previously reported by us for the free radical polymerization of VK in a large number of solvents[6]. The virtual polymerization temperature independence of the steric microstructure of the cationically polymerized component was consistent with the situation encountered in the BF_3OEt_2-catalysed cationic polymerization of VK in dichloromethane (see *Table 4*). Furthermore *Table 4* shows that the steric microstructure of PVK cationically polymerized in dichloromethane is remarkably insensitive to changes in counterion. Since the data in *Table 4* includes X_i data for the tropylium hexachloroantimonate catalysed cationic polymerization of VK whose propagation has been shown to involve free cations[13], one must assume that a large degree of ion-pair dissociation is also present in the BF_3OEt_2-catalysed and photoinitiated cationic polymerization of VK in dichloromethane. This would explain the temperature independence of the steric microstructure, since at large ion-pair separations the steric configuration during the propagation process will be relatively unaffected by changes in solvation due to changes in temperature.

The question of which species initiates the free radical

Table 4 Polymerization conditions and steric microstructures of the cationically polymerized component compared with several BF_3OEt_2 and $C_7H_7^+SbCl_6^-$ catalysed cationically polymerized PVK samples

Polymer No.	Polymerization temperature (°C)	Counterion	Diad mole fractions$^+$	
			X_i	X_s
UV59	−80	$CH_2Cl_2^- \cdot$ or Cl^-	0.44	0.56
2B and 3B	−69	$BF_3O(C_2H_5)(C_2H_4^-)$	0.45	0.55
UV86	−3	$CH_2Cl_2^- \cdot$ or Cl^-	0.45^5	0.54^5
1C	0	$SbCl_6^-$	0.42*	0.58*
UV87	+25	$CH_2Cl_2^- \cdot$ or Cl^-	0.46^5	0.53^5
8B	+42	$BF_3O(C_2H_5)(C_2H_4^-)$	0.42	0.58

$^+$ From T_g measurements
* From ^{13}C n.m.r. measurements

polymerization, either in the presence or absence of free radical photoinitiators, cannot be categorically answered. In the presence of BME, initiation probably proceeds predominantly *via* the direct photolytic decomposition of BME, since the BME absorption at 366 nm (ε_{BME} at 366 nm = 94 dm^3 mol^{-1} cm^{-1}) was between 26 and 82% of the total absorption. However, in the presence of AIBN an indirect photolytic decomposition of AIBN via energy transfer from the VK singlet, such as that proposed by Jones *et al.*[14] for the analogous process in benzene solution, was indicated by the polymerization yields obtained. Thus at +15°C photopolymerization in the presence of AIBN absorbing 6% of the incident light produced a yield of 78% after 2 h polymerization, which compared with 47% after 2 h obtained in the presence of BME absorbing 26% of the incident light, despite the photolytic quantum efficiencies for AIBN and BME being similar[15,16].

The free radical photoinitiation of VK polymerization in the absence of photoinitiators must involve either directly or indirectly the VK triplet or the VK radical cation. Should free radical initiation occur exclusively *via* the VK radical cation, then one would expect that the ratio of the number of free radically to cationically polymerized polymer chains would be virtually temperature independent, since both cationic and free radical initiation would involve the same species. In fact this ratio was found to increase from *ca.* 0.1 at +26°C to 3.2 at −36°C, which would suggest that free radical initiation takes place via another species.

CONCLUSION

At polymerization temperatures above −5°C, the photopolymerization of VK in the presence of BME and AIBN was much faster than that in the absence of such free radical photoinitiators and moreover proceeded exclusively free radically. Below this temperature in the presence of BME or AIBN and below 26°C in the absence of free radical photoinitiators, simultaneous but separate free radical and cationic polymerization took place.

The activation enthalpy difference between isotactic and syndiotactic polymerization, $(\Delta H^{\ddagger}_{s/i} - \Delta H^{\ddagger}_{i/s})$, for the free radically and cationically polymerized components of the PVK samples were −2.65 kJ mol^{-1} and +260 J mol^{-1} respectively. The former is consistent with $(\Delta H^{\ddagger}_{s/i} - \Delta H^{\ddagger}_{i/s})$ data previously reported for the free radical polymerization of VK in a variety of solvents[6]. The virtual temperature independence of the steric microstructure of the cationically polymerized component was due to the ion-pair separation being sufficiently large in dichloromethane so as not to be influenced by the temperature dependent variation in solvation.

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