Radical polymerizations of some vinyl alkyl carbonates

John R. Ebdon*
The Polymer Centre, School of Physics and Materials, Lancaster University, Lancaster LA1 4YA, UK

and Inger Reidun F. Aukrust, Keith Redford and Jan Solberg
SINTEF, PO Box 124 Blindern, N-0314 Oslo, Norway
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Some simple experiments have been carried out to assess the kinetics of the radical polymerizations of vinyl ethyl, vinyl tert-butyl, vinyl phenyl and vinyl benzyl carbonates at temperatures between 30°C and 60°C. It is shown that, contrary to some impressions given in the literature, the vinyl alkyl carbonates can be polymerized readily to give polymers of high molecular weight with conventional radical initiators (i.e. benzoyl peroxide and azoisobutyronitrile) provided that it is recognized that they polymerize relatively slowly owing, probably, to them having relatively low values of $k_p/k_t^{1/2}$. Therefore radical initiators must be used with these monomers at temperatures at which they will have relatively long half-lives. It is further shown that the low-temperature initiator, dicyclohexylperoxydicarbonate (DCHPC), favoured by previous workers for the polymerization of these monomers, offers no obvious advantages over the use of the more conventional initiators at higher temperatures, and that an alternative low temperature initiator, tert-butylperoxyneodecanoate, polymerizes vinyl alkyl carbonates with a facility equal to that of DCHPC.

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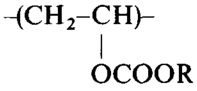
INTRODUCTION

The poly(vinyl alkyl carbonate)s (I), unlike the poly(vinyl alkyl ester)s to which they bear a structural similarity, are a relatively little explored group of polymers.



$$\left(\underset{\displaystyle \text{OCOOR}}{CH_2-\underset{|}{CH}}\right) \qquad (I)$$

In part this is probably because the monomers from which they are made are not generally available. However, following some pioneering experiments carried out by Schaefgen[1,2] in which vinyl tert-butyl carbonate was polymerized at −50 and −80°C using tri-n-butyl boron as initiator, Boileau and co-workers have more recently described the production of poly(vinyl alkyl carbonate)s of high molecular weight by radical polymerizations in bulk monomer or in solutions in benzene or methylene chloride using azoisobutyronitrile (AIBN), benzoyl peroxide (BPO), dicyclohexylperoxydicarbonate (DCHPC) and bis-tert-butyl dicyclohexylperoxydicarbonate (TBDCHPC) as initiators[3–7]. Of these initiators, Boileau and co-workers seem to favour the low temperature initiators, DCHPC and TBDCHPC, owing to their apparent ability to give higher molecular weight polymers in higher yields than can be achieved with AIBN and BPO. Freire *et al.* have also prepared polymers from various vinyl alkyl carbonates, using TBDCHPC as initiator, and have measured their glass transition temperatures (T_gs) and related these to the structures of the polymers[8]. Gibson and Kurek, however, have reported an inability to produce polymer from vinyl tert-butyl carbonate at 60°C using AIBN as initiator although polymer was produced successfully from this monomer at this temperature, and lower, again using DCHPC[9].

On reading these various reports it seemed to us unlikely that DCHPC and TBDCHPC were unique in their ability to produce high molecular weight polymers from vinyl alkyl carbonates at modest temperatures and also unlikely that these initiators offered any real advantage over more conventional initiators (such as AIBN and BPO) used at higher temperatures, unless it so happens that the ceiling temperatures for radical polymerizations of the monomers are rather low. With these thoughts in mind, we have carried out some simple experiments to estimate rate constants at various temperatures for the radical polymerizations of some vinyl alkyl carbonates.

EXPERIMENTAL

Materials

Vinyl ethyl carbonate (VEC), vinyl tert-butyl carbonate (VTBC), vinyl phenyl carbonate (VPC) and vinyl benzyl carbonate (VBC) were synthesized from vinyl chloroformate (Jannsen, 99%) by reaction with the

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* To whom correspondence should be addressed

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appropriate alcohol following essentially procedures first given by Schnur[10]. Brief details follow.

VEC. To a solution of vinylchloroformate (6.58 g, 0.07 mol) and ethanol (3.22 g, 0.07 mol) in methylene chloride (100 ml), pyridine (5.54 g, 0.07 mol) was added over a period of 45 min at 0°C. The temperature was then raised to 25°C and after 4 h the reaction mixture was filtered and the solvent was removed under reduced pressure. A final distillation on the vacuum line gave 1.95 g (24%) of the title product. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 1.21 (t, 3H, CH_3), 4.15 (q, 2H, $\underline{CH_2}CH_3$), 4.41 (dd, 1H, $CH_2{=}$), 4.74 (dd, 1H, $CH_2{=}$), 6.97 (dd, 1H, $CH{=}$). ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 14.50 (CH_3), 64.90 (CH_2), 97.64 ($CH_2{=}$), 142.99 ($CH{=}$), 152.45 ($C{=}O$).

VTBC. Preparation was as for VEC except for the use of 0.05 mol of each of vinylchloroformate, tert-butanol and pyridine. Removal of the solvent under vacuum, followed by vacuum distillation at 32°C, gave 4.3 g (56%) of the title product. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.45 (s, 12H, CH_3), 4.48 (dd, 1H, $CH_2{=}$), 4.82 (dd, 1H, $CH_2{=}$), 7.05 (dd, 1H, $CH{=}$).

VPC. Preparation was as for VEC except for the use of 0.12 mol of each of vinylchloroformate, phenol and pyridine, 150 ml methylene chloride, and addition of pyridine at −10°C. After removal of the solvent, flash chromatography (silica/methylene chloride) gave 15.15 g (77%) of the title product. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 4.71 (dd, 1H, $CH_2{=}$), 5.05 (dd, 1H, $CH_2{=}$), 7.30 (m, 6H, $CH{=}$ + Ar). ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 99.27 ($CH_2{=}$), 121.34, 126.80 and 129.98 (Ar.CH), 142.84 ($CH{=}$), 150.85 (Ar.C), 151.62 ($C{=}O$).

VBC. Preparation was as for VPC except for the addition of pyridine at 0°C. Flash chromatography gave 16.0 g (75%) of the title product. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 4.60 (dd, 1H, $CH_2{=}$), 4.95 (dd, 1H, $CH_2{=}$), 5.24 (s, 2H, O-$\underline{CH_2}$-Ph), 7.14 (dd, 1H, $CH{=}$), 7.40 (m, 5H, Ar). ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 71.03 (CH_2), 98.51 ($CH_2{=}$), 128.83, 129.04 and 129.13 (Ar.CH), 135.00 (Ar.C), 142.90 ($CH{=}$), 152.84 ($C{=}O$).

AIBN (Janssen, 98%) was purified by dissolution in the minimum amount of chloroform followed by reprecipitation in an equal amount of petroleum ether. BPO (Merck, >98%) was purified by dissolution in the minimum amount of chloroform followed by reprecipitation in the same amount of methanol. Both initiators were dried by pumping under vacuum at room temperature and stored at 4°C prior to use. The low temperature initiator, tert-butyl peroxyneodecanoate (TBPD) (Trigonox 23-C75, Akzo), was used without purification. Stock solutions of this initiator in benzene were made up as required and stored at −20°C prior to use.

Polymerizations

Polymerizations were carried out on solutions of monomers in benzene in sealed ampoules under vacuum at temperatures between 30°C and 60°C using AIBN, BPO and TBPD as initiators. Benzene was chosen as the solvent so as to minimize the possibilities for chain transfer. The appropriate amounts of initiator and solvent were put into the ampoule first, followed by the required amount of monomer. The monomer was either introduced directly (in the cases of VTBC, VPC and VBC) or distilled in on the vacuum line (in the case of VEC). The ampoules were degassed before sealing using the usual freeze–pump–thaw cycles (×4). With the exception of poly(VTBC), polymers were recovered from the ampoules by precipitation in petroleum ether and were freed from monomer and benzene by repeated washings, with vigorous stirring, with petroleum ether. The polymers were then dried by pumping on the vacuum line at ~100°C for 3–4 h. The poly(VTBC) samples could not be precipitated satisfactorily in petroleum ether and were therefore recovered by removal of the bulk of the solvent and residual monomer on a rotary evaporator followed by further drying on the vacuum line at 100°C. Even so, significant amounts of monomer (~10% w/w) remained in the polymers. Allowance for this residual monomer (quantified by ^{1}H n.m.r. analysis of the polymers in $CDCl_3$) was made when calculating the yields of poly(VTBC).

Molecular weight measurements

Molecular weights and polydispersities were measured on solutions of polymers in tetrahydrofuran (THF) by g.p.c. using a Waters chromatograph equipped with Polymer Laboratories columns (1 × 30 cm containing 10 μm particle size, 500 Å pore size, PLgel™ plus 1 × 30 cm containing 10 μm particle size, 10^4 Å pore size, PLgel™) and operated with the aid of Polymer Laboratories Caliber™ software. The columns were calibrated over the molecular weight range 372–980 000 using a set of narrow molecular weight polystyrene standards. Solvent flow rate was 1 ml min^{-1}.

RESULTS

Polymerizations of VEC, VTBC, VPC and VBC were carried out to moderate conversions in benzene at various temperatures, T, for various times, t. The yields of the polymers were recorded and used to calculate rates of polymerization, R_p. These rates together with the monomer concentrations, [M], and initiator concentrations, [I], are collected in *Table 1*. Also given in *Table 1* are number-average molecular weights, M_n, and polydispersities, D, obtained by g.p.c.

All of the polymers were white, and were soluble in a variety of solvents including benzene, methylene chloride and THF.

DISCUSSION

In order to compare the polymerization data for the vinyl alkyl carbonates with those for other, more conventional monomers, such as vinyl acetate, methyl methacrylate and styrene, we have made some assumptions about the free radical processes. These are that in all cases polymerization follows classical radical kinetics with termination by disproportionation and no transfer. These assumptions allow us to calculate the ratio $k_p/k_t^{1/2}$ in the classical equation for ideal radical polymerizations:

$$R_p = (k_p/k_t^{1/2})[M](2fk_d[I])^{1/2} \qquad (1)$$

where k_p, k_t and k_d are the rate constants for propagation, termination and initiator decomposition, respectively, and f is the initiator efficiency. Having obtained $k_p/k_t^{1/2}$ values from the measured R_p values, we can then calculate

Table 1 Details of polymers prepared

Monomer	T (°C)	Initiator	[I] (mol $l^{-1} \times 10^3$)	[M] (mol l^{-1})	t (h)[a]	Conversion (%)[a]	R_p (mol l^{-1} $s^{-1} \times 10^5$)	M_n	D
VEC	30	TBPD	4.10	5.69	20	3	0.224	21 600	1.96
VTBC	60	AIBN	8.05	3.26	6	12	1.862	62 700	1.75
	50	AIBN	6.10	3.26	24	12	0.477	65 400	2.25
	30	TBPD	4.10	3.26	20	4	0.172	45 900	1.78
VPC	60	BPO	12.89	3.38	8	11	1.366	23 500	1.84
	60	AIBN	6.10	3.38	19	22	1.090	32 400	1.61
	50	AIBN	6.10	3.38	19	6	0.276	42 600	1.95
	50	AIBN	8.05	3.38	18	6	0.315	34 500	1.87
	35	TBPD	17.10	3.38	39	24	0.578	27 800	1.96
	35	TBPD	17.10	3.38	16	9	0.516	30 200	1.77
	30	TBPD	4.10	3.38	20	3	0.139	31 900	2.07
VBC	60	AIBN	6.10	3.06	17	35	1.573	23 500	1.93
	60	AIBN	7.56	3.06	8	20	2.230	23 300	1.82
	30	TBPD	4.10	3.06	21	3	0.134	20 500	1.79

[a] These figures have been rounded to the nearest integer; in calculating R_p values, precise yields and reaction times were used

Table 2 Calculated kinetic parameters for polymerizations of VEC, VTBC, VPC and VBC

Monomer	T (°C)	Initiator	$k_p/k_t^{1/2}$ ($l^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$)	M_n
VEC	30	TBPD	0.003_{38}	19 170
VTBC	60	AIBN	0.019_{56}	31 540
	50	AIBN	0.011_{27}	40 060
	30	TBPD	0.003_{88}	15 690
VPC	60	BPO	0.017_{79}	43 440
	60	AIBN	0.011_{06}	21 020
	50	AIBN	0.006_{30}	26 920
	50	AIBN	0.006_{25}	23 290
	35	TBPD	0.004_{13}	5520
	35	TBPD	0.003_{68}	4920
	30	TBPD	0.003_{32}	15 840
VBC	60	AIBN	0.019_{02}	40 820
	60	AIBN	0.025_{79}	49 720
	30	TBPD	0.003_{78}	17 680

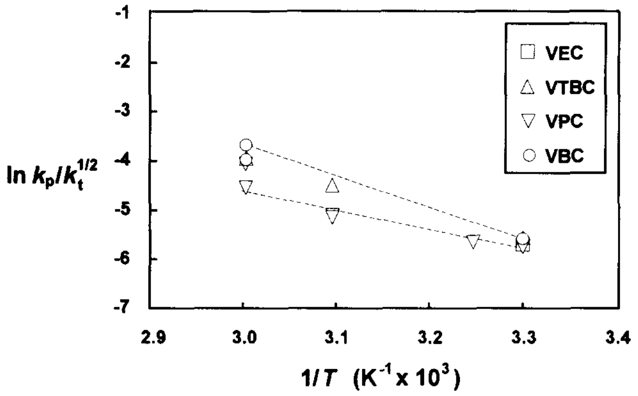

Figure 1 Plots of ln $k_p/k_t^{1/2}$ *versus* $1/T$ for VEC, VTBC, VPC and VBC. The data are taken from *Table 2* and the broken lines show lines of possible maximum and minimum slope that may be drawn through the points to evaluate activation energies (see text for details)

the expected values of M_n using the equations:

$$P_n = v_n = (k_p/k_t^{1/2})[M]/(2fk_d[I])^{1/2} \quad (2)$$

and

$$M_n = P_n \times m \quad (3)$$

where P_n is the number-average degree of polymerization, v_n is the kinetic chain length and m is the molecular weight of the monomer unit. [Note that in deriving equations (1) and (2), the termination step, $-d[R^\bullet]/dt$, has been defined as $k_t[R^\bullet]^2$ rather than as $2k_t[R^\bullet]^2$ so as to produce $k_p/k_t^{1/2}$ values that can be directly compared with those in the literature which have mostly been derived assuming the former convention[14].]

Table 2 contains the results of applying equations (1) and (2) to the data contained in *Table 1*. For the decompositions of BPO at 60°C and AIBN at 60°C and 50°C, the k_d values have been assumed to be 2.14×10^{-6}, 8.80×10^{-6} and 2.30×10^{-6} s^{-1}; these are averages of values given in reference 11 for decompositions of these initiators at the relevant temperatures in benzene or toluene. For TBPD we have calculated k_d values at 35 and 30°C using a k_d value of 1.9×10^{-5} s^{-1} at 47°C given in reference 11 together with information from the manufacturer[12] that at 100°C the half-life, $t_{1/2}$, for TBPD is 75 s, and assuming that initiator decomposition is a first-order process, i.e. that:

$$k_d = \ln 2/t_{1/2} \quad (4)$$

The values of f have been assumed to be 1.0, 0.6 and 1.0 for BPO, AIBN and TBPD, respectively. The f values for BPO and AIBN are those normally assumed for these initiators[13]; for TBPD there is no information available.

In *Figure 1*, values of ln $k_p/k_t^{1/2}$ are plotted against $1/T$. The points for VPC (with the exception of that for VPC initiated with BPO at 60°C) lie close to a line, the slope of which gives $E_p - \frac{1}{2}E_t = 30$ kJ mol^{-1}, where E_p is the activation energy for propagation and E_t is that for termination. The data for the other vinyl alkyl carbonates are distributed about a line of slightly greater slope, giving $E_p - \frac{1}{2}E_t = 47$ kJ mol^{-1}. These values can be compared with those given in reference 14 (18–34 kJ mol^{-1}) for vinyl acetate, a monomer with a structure similar to that of the vinyl carbonates.

It is interesting to consider at this point polymerization data for VPC published by Boileau and co-workers[6]. Boileau *et al.* polymerized VPC in bulk using BPO at 87 and 80°C and DCHPC at 35°C. Estimates of $k_p/k_t^{1/2}$ values from their BPO data are very low compared with ours (e.g. $0.0047\,\mathrm{l}^{1/2}\,\mathrm{mol}^{-1/2}\,\mathrm{s}^{-1/2}$ at 80°C). The reason for this is the one recognized by Boileau *et al.*, namely that at these temperatures, the polymerizations are exhibiting 'dead-end' characteristics[15], i.e. the initiator is decomposing too quickly given the long polymerization times required to obtain reasonable yields of polymers. (At temperatures above 80°C, the half-life of BPO is <5 h.) From the published results for the two polymerizations carried out with DCHPC at 35°C, on the other hand, we estimate, using k_d values and an activation energy for DCHPC decomposition obtained from reference 11 and assuming that $f=1$, $k_p/k_t^{1/2}$ values of 0.0057 and $0.0135\,\mathrm{l}^{1/2}\,\mathrm{mol}^{-1/2}\,\mathrm{s}^{-1/2}$, respectively. Although these values are not self-consistent, possibly because the high concentration of DCHPC used in the second experiment (0.5% of the monomer concentration) led to some induced decomposition of the initiator of the type described by Van Sickle[16], the first value of $k_p/k_t^{1/2}$ is reasonably close to that obtained by us at 35°C using TBPD (*Table 2*). At 35°C, the half-lives of DCHPC and TBPD are 29 and 55 h, respectively.

The calculated values of M_n given in *Table 2* are to be compared with those measured and given in *Table 1*. Bearing in mind the uncertainties, approximations and assumptions in the kinetic treatment, the agreement between the calculated and measured values of M_n can be regarded as satisfactory. In all but two cases, the measured M_n value is within an order of magnitude of the calculated one. The exceptions are the two polymerizations of VPC at 35°C using relatively high concentrations of TBPD. For these polymerizations, the measured M_n values are much higher than expected, possibly indicating wastage of initiator through induced decompositions leading to non-radical products (i.e. that $f \ll 1$ under these conditions).

It would seem from our data therefore that, contrary to impressions given in the literature, there is nothing especially remarkable or unusual about the radical polymerizations of the four vinyl alkyl carbonates, except that they all have low values of $k_p/k_t^{1/2}$ (roughly an order of magnitude lower than those of many common monomers, including vinyl acetate which could be regarded as structurally similar[14]). This low reactivity in polymerization can be seen also, indirectly, in copolymerizations of VPC and vinyl acetate (VA) for which $r_{VPC}=0.38$ and $r_{VA}=0.83$ have been reported[7].

Provided that properly purified monomers are used, and that polymerizations are carried out with the rigorous exclusion of oxygen, e.g. under vacuum, satisfactory polymers can be obtained using conventional radical initiators at the normally convenient temperatures, even from VTBC. We believe the reason why Gibson and Kurek failed to obtain poly(VTBC) at 60°C using AIBN[9] is that they attempted to precipitate the polymer in petroleum ether. We have found that VTBC reaction mixtures do not precipitate properly in petroleum ether, but produce only a transient turbidity. We ascribe this to the fact that petroleum ether is probably not as good a non-solvent for this polymer as it is for poly(VEC), poly(VPC) and poly(VBC).

However, it should be recognized that, owing to the low $k_p/k_t^{1/2}$ values and to avoid 'dead-end' characteristics, conventional initiators are best used with the vinyl alkyl carbonates at temperatures at which their half-lives are in the range of 50–100 h. This means that AIBN is perhaps best employed at 50°C (at which $t_{1/2}$ is 84 h) rather than at the more usual 60°C (at which $t_{1/2}$ is 22 h) and that BPO is best used at $\sim$60°C (at which $t_{1/2}$ is 90 h) rather than at the more usual 80°C (at which $t_{1/2}$ is only just over 5 h). The molecular weight of the polymer will of course be controlled largely by the ratio of [I] to [M] in the usual way, and thus the preparation of high molecular weight polymers will require low [I] and hence, unavoidably, relatively long polymerization times. Under these circumstances, it becomes even more important to use an initiator with a reasonably long half-life at the chosen polymerization temperature.

Finally, it is to be noted that there appears to be nothing special about DCHPC (and, by implication, also TBDCHPC) as initiators for the low temperature radical polymerization of vinyl alkyl carbonates; the low temperature initiator TBPD works equally well.

CONCLUSIONS

Vinyl alkyl carbonates can be polymerized free radically to give good yields of high molecular weight polymer provided it is recognized that rates of polymerization will be low, owing to low values of $k_p/k_t^{1/2}$, and therefore that an initiator is used that has a sufficiently long half-life (say, 50 h or more) at the chosen polymerization temperature.

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