Reaction of 2,4-dinitrophenylhydrazine with methylvinylketone copolymers. Effect of steric environment

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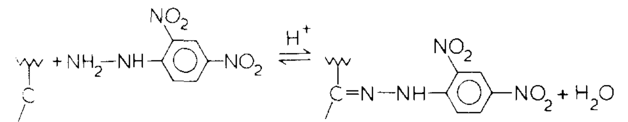
The reaction of 2,4-dinitrophenylhydrazine (DNPH) with methylvinylketone copolymers of styrene, methylacrylate, methylmethacrylate and cyclohexylmethacrylate has been studied. The equilibrium nature of the reaction is clearly observable leading to non-quantitative reactions under all conditions investigated. The equilibrium constant (*K*) for hydrazone formation decreases in the order methylacrylate > styrene ≫ methylmethacrylate > cyclohexyl methacrylate indicative of pronounced steric effects. The temperature dependence of *K* reveals that the reaction is thermodynamically, rather than kinetically, controlled.

Keywords Dinitrophenylhydrazine; steric environment; methylvinylketone; thermodynamics; copolymer; equilibrium

Introduction

The reaction of 2,4-dinitrophenylhydrazine (DNPH) with carbonyl groups (equation (1)) has been widely used[1-4] as the basis for the estimation of the ketone and aldehyde content of polymers. Recently, however, it has been shown[4] that in the case of carbonyl groups in styrene/methylvinylketone copolymers the above reaction is not quantitative, since the equilibrium lies heavily to the left-hand side of equation (1) under normal experimental conditions. This observation has prompted us to probe the influence of the steric environment of the ketone functional group on the above reaction.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To study these effects, a series of copolymers of methylvinylketone (MVK) with various comonomers has been prepared. A known steric environment, i.e., isolated ketone repeating units, was assured by the use of only trace amounts (*ca.* 1 mole%) of MVK in the copolymer. The prepared ketone copolymers were reacted with DNPH under standardized conditions, and the extent of reaction monitored by u.v. analysis. The nature of the steric environment was found to have a profound effect on the extent of hydrazone formation.

Experimental

Materials. Monomers and solvents were high quality grades, were purified by standard procedures, distilled and dried over 3 Å molecular sieves[5]. Tritium labelled MVK, specific activity 7.41×10^8 dpm mol^{-1}, was synthesized as described earlier[6].

Copolymer synthesis and analysis. Copolymers of MVK were prepared by heating a mixture of ^{3}H-labelled MVK (0.0012 mole), comonomer (0.12 mole), and benzoyl peroxide (0.2 g), diluted to 35 ml with toluene, at 60°C for 16 h. Copolymers were isolated by precipitation into excess methanol and purified by subsequent reprecipitation from dichloromethane, followed by vacuum drying. The carbonyl content was accurately determined (within ±2%) by a radiotracer method detailed elsewhere[6].

Reaction of DNPH with copolymers. Copolymer (0.2 g) and DNPH (0.1 g) were dissolved in a solvent mixture of toluene (20 ml) and DMF (5 ml) in the presence of conc. hydrochloric acid (10 μl). After heating at temperatures specified in the text the reacted copolymer was isolated by methanol precipitation and purified by three further reprecipitations from chloroform. DNPH incorporation was determined by u.v. analysis as previously described[4], using a value of $\varepsilon = 1.97 \times 10^4$ at $\lambda_{\max} = 360$ nm.

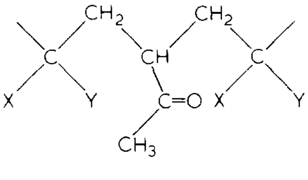
Results and Discussion

Preliminary investigations. General aspects of the DNPH reaction were examined using a methylmethacrylate (MMA) copolymer. The use of a mixed solvent system toluene/DMF has been continued from earlier published work[7] concerned with carbonyl determination in oxidized rubbers. Experiments omitting DMF show that, whereas, the copolymers are readily soluble in toluene alone, the DMF is necessary for the effective dissolution of the DNPH.

Hydrazone formation is known to be subject to acid catalysis[8] and earlier work has shown[4] that the extent of reaction of DNPH with carbonyl (aldehydic) groups in natural rubber is somewhat dependent on pH. Comparison of the reaction of DNPH with carbonyl groups in the MMA/MVK copolymer, at 100°C for 1 hour, in the presence and absence of acid, shows that in the latter case, incorporation is negligible (<1% of the acid catalysed value). This clearly demonstrates that the reactivity of ketonic carbonyl groups is crucially dependent on the presence of acid, in contrast to the only moderate dependence with the more reactive aldehydic carbonyl groups[4].

Treatment of a MMA homopolymer with the acidified DNPH reagent showed no reaction, hence ruling out the possibility of DNPH exchange with polymeric ester groups, in the experiments reported below.

Effect of polymer structure. The environment of the reactive carbonyl group is represented schematically below: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By variation of the nature (size) of the substituent groups X, Y it is possible to change the steric crowdedness of the carbonyl group. In these experiments the effect of monosubstituted monomers (methylacrylate, styrene) and disubstituted monomers (methylmethacrylate and cyclohexylmethacrylate) were probed. It can be readily seen (*Figure 1* and *Table 1*) that the extent of reaction with DNPH is largely controlled by steric effects. Thus, the disubstituted monomers give rise to a crowded steric environment which is unfavourable for formation of the bulky DNPH derivative. This is reflected in lower equilibrium constants (K) for these systems.

It is noticeable that moving from a monosubstituted monomer (methyl acrylate) to the disubstituted analogue (methylmethacrylate) has a much more dramatic effect on K than increasing the bulk of one of the disubstituted groups (e.g., cyclohexylmethacrylate).

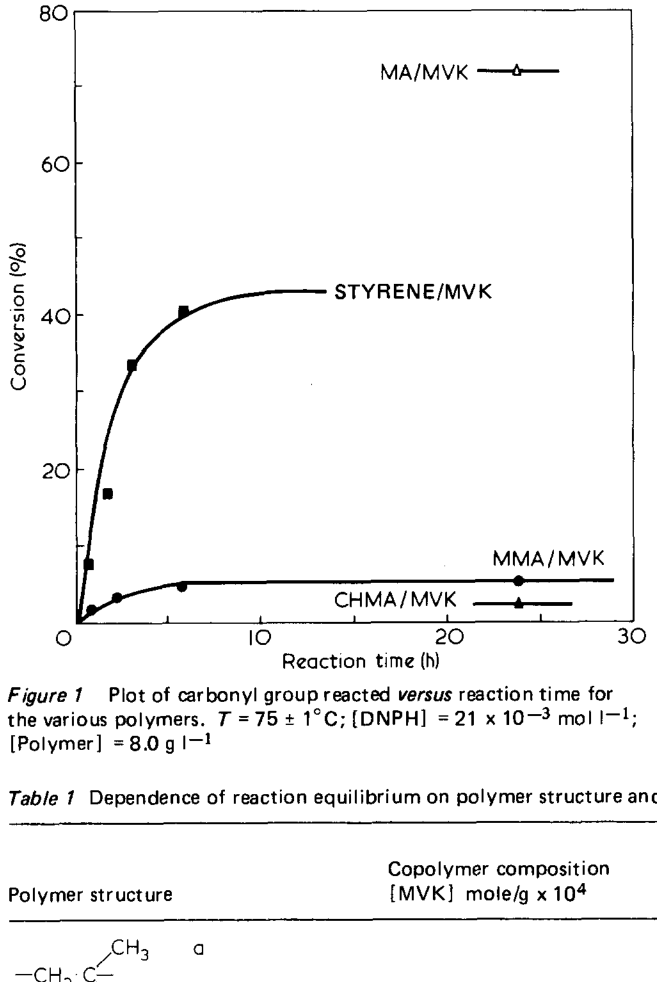

Figure 1 Plot of carbonyl group reacted *versus* reaction time for the various polymers. $T = 75 \pm 1°C$; $[DNPH] = 21 \times 10^{-3}$ mol l^{-1}; [Polymer] $= 8.0$ g l^{-1}

For all copolymers the reactions are found to be far from quantitative at 75°C ranging from about 72% conversion (MA copolymer) to as little as 3% conversion for the CHMA copolymer.

Effect of temperature. In attempting to promote a reaction by increased temperature, possible conflicts of kinetic and thermodynamic parameters must not be overlooked, as apositely illustrated in the systems under study. Thus, although the rate of attainment of equilibrium is enhanced at higher temperatures, the position of the equilibrium is shifted to the left-hand side of equation (1), due to decreasing K values (*Table 1*).

Although the reproducibility of individual equilibrium constants is rather poor ($\pm 10\%$), at the low carbonyl concentrations used in this study, the order of magnitude of the thermodynamic parameters (ΔH and ΔS) may be derived from the dependence of K upon temperature, making the usual assumption that the enthalpy is temperature independent over the range of interest. For the methylmethacrylate copolymer, values of $\Delta H = -81$ kJ mol^{-1} and $\Delta S^{333} = -230$ J K^{-1} mol^{-1} are obtained.

These results clearly show that whereas the reaction is favoured by the enthalpy change, the large negative entropy of reaction is strongly inhibitive for these sterically crowded polymeric systems.

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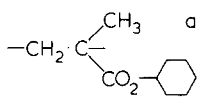
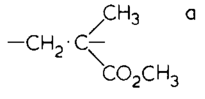
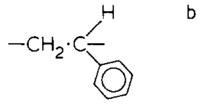
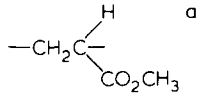
Table 1 Dependence of reaction equilibrium on polymer structure and temperature

Polymer structure	Copolymer composition [MVK] mole/g x 10^4	K (l mol^{-1}) 60 ± 1°C	75 ± 1°C	90 ± 1°C	100 ± 1°C
 a	0.491	4.4	1.5	–	–
 a	1.28	6.3	2.5	0.61	0.35
 b	2.47	100	37	10	7.6
 a	1.59	186	122	–	–

K values determined at: a – 24 h; b – 6 h. As earlier[4] $K = \dfrac{[C{=}N]_{eq}}{[C{=}O]_{eq}\,[DNPH]_{eq}}$