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The Synthesis and Polymerisability of Methyl-2-(Methacroyloxy)ethyl Terephthalate. A Useful Free Radically-Polymerisable Model for Dimethylterephthalate

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Summary

The synthesis of methyl-2-(methacroyloxy)ethyl terephthalate is described. This monomer is an electron acceptor which quenches the fluorescence of excited donor molecules and serves as a free radically polymerisable model for dimethyl terephthalate.

Dimethyl terephthalate (DMT) is a weak electron acceptor and a highly efficient quencher for the fluorescence of a number of electron donor species, especially carbazole derivatives (Yamamoto et al 1969, Nishijima et al 1972, Tazuke et al 1975). The interactions of electronically excited carbazoles with ground state DMT are characterised, in favourable circumstances, by the appearance of broad, structureless, fluorescence emission bands lower in energy than the corresponding carbazole fluorescence (Hoyle and Guillett, 1978). Excited states responsible for the low energy emission bands are assumed to be exciplexes formed by collisional interaction of singlet excited carbazole with ground state DMT:

$$\begin{tikzcd}
 & & \text{Carbazole + DMT} \\
\text{Carbazole} \arrow[r, "h\nu"] & \text{Carbazole}^* \arrow[r, "\text{DMT}"] \arrow[d, "-h\nu"] & \underset{\text{exciplex}}{[\text{Carbazole, DMT}]^*} \arrow[u] \arrow[d, "-h\nu'"] \\
 & \text{Carbazole} & \text{Carbazole + DMT}
\end{tikzcd}$$

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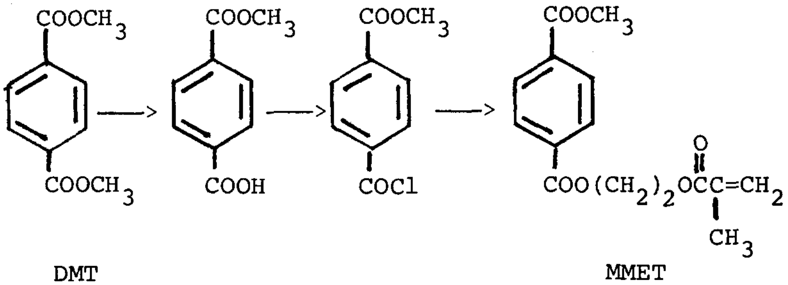
Tazuke and Matsuyama (1975, 1976) have synthesised a number of copolymers, having in-chain terephthalate groups and pendent carbazole moeities, by step growth condensation of terephthalic acid with suitable functionalised carbazoles, all of which have interesting exciplex emission properties. Apparently intermacromolecular exciplex emission is important only at relatively high molecular weights which, in the case of the step growth polymers from terephthalic acid, implies that $\overline{DP} \gg 10$. This interesting result has stimulated further experimental work because of the apparent difficulty experienced in synthesising copolymers with $\overline{DP} > 10$.

Higher molecular weights would be expected for appropriately functionalised co-polymers derived by chain-growth polymerisation and, for this purpose, it was necessary to synthesise a suitable derivative of terephthalic acid; N-vinylcarbazole (NVC) is a readily available vinyl monomer having the desired carbazole electron-donor capability.

In this paper we report a convenient synthesis and the polymerisability of methyl-2-(methacroyloxy)-ethyl terephthalate (MMET).

Synthesis of the mono-acidchloride from DMT was carried out according to the literature method (Frazer, 1969) and MMET was obtained by the following reaction sequence:



Free radical homopolymerisation of MMET was readily accomplished using AIBN as initiator and the homopolymer ($\overline{M}_n$ = 190,000) has T_g = 341K (D.S.C) which is somewhat lower than that for an equivalent sample of poly(methylmethacrylate) for which T_g = 387K.

MMET is a suitable vinyl-polymerisable model for DMT, which readily copolymerises to high molecular weight products with the usual range of vinyl monomers. In particular MMET copolymerises free radically with NVC to give polymers having strong exciplex emission characteristics which will be described in a separate publication.

4-(Carbomethoxy)benzoic acid. A solution of 97.0g (0.5 mol) of dimethyl terephthalate (DMT) in 300ml of dichloromethane was mixed with 200ml of methanol. To the resulting clear solution, a solution of 38.0g (0.57 mol) of potassium hydroxide in 150ml of methanol, was added dropwise, with stirring. The potassium salt started to separate during the addition, and the resulting suspension was stirred at room temperature for 24 hours before the salt was filtered, washed with a small volume of methanol, and dissolved in 500ml of water. After acidifying the aqueous solution, the solid acid was filtered and recrystallized from alcohol-water (50:50), yielding 72g (80%) of 4-(carbomethoxy)benzoic acid m.p. 220-222° [Frazer 1969, m.p. 220-222°].

4-(Carbomethoxy)benzoyl chloride. A mixture of 65.0g of dry 4-(carbomethoxy)benzoic acid and 500ml of thionyl chloride was refluxed for 24 hours. The excess thionyl chloride was evaporated *in vacuo*, leaving a crystalline residue which was recrystallized from cyclohexane to give 52g (72.5%) of a colourless crystalline product, m.p. 51-52° [Frazer, 1969, m.p. 54°], b.p. 142-3°.

Methyl-2-(methacroyloxy)ethyl terephthalate (MMET) A solution of 19.85g (0.1 mol) 4-(carbomethoxy)benzoyl chloride in 100ml dry dioxane was added dropwise with stirring to a solution of 16.0g (0.12 mol) of 2-hydroxyethyl methacrylate and 12ml (0.09 mol) of triethylamine in 100ml dry dioxane. The temperature was controlled by means of an ice bath and did not rise above 6°C during the addition, after which the mixture was stirred for two hours at approximately 10°C followed by a further one half hour stirring at room temperature. The mixture was filtered, the filtrate poured into 100ml dilute hydrochloric acid, and extracted with three 100ml portions of diethyl ether. The combined ethereal extracts were evaporated to dryness *in vacuo*, leaving an oily residue, which was taken into 100ml of 80% water-methanol saturated with sodium bicarbonate and stirred at room temperature overnight. This mixture was then diluted with water and extracted with three 100ml portions of diethyl ether, the ether extracts were combined, washed with water, dried (M_gSO_4) and evaporated *in vacuo*, leaving 17.2g (59%) of a colourless oily residue (m.p. *ca* 17°C). The product which showed only one spot on t.l.c. was carefully dried, protected from light and heat and kept under nitrogen. Found: C, 61.60%; H, 5.68%. $C_{15}H_{16}O_6$ requires: C, 61.63%; H, 5.52%. Infra red; ν_{max} 2960 (C-H), 1720 (C=O), 1630 (C=C), 1435, 1410, 1270, 1165, 1100, 1020 and 730 cm^{-1}. N.M.R; τ ($CDCl_3$) 1.73 (4H, s, ArH), 369 (1H, m, olefinic proton), 4.23 (1H, m, olefinic proton), 5.24 (4H, s, 2 x CH_2), 5.9 (3H, s, $COOCH_3$), 7.89 (3H, m, CH_3). Mass Spec; m/e 163 $[(M - O(CH_2)_2\text{-}OCOC(CH_3){=}CH_2]^+$ (100%); 292 (M^+, 0.19); 261 (2.51); 207 (3.77); 111.8 (M^*, 163-135).

Poly[methyl-2-(methacroyloxy)ethyl terephthalate]

Homopolymerisation of MMET was carried out by the usual procedure. 1g of MMET in 5ml of dichloromethane containing 10mg AIBN was outgassed and heated at 55°C for 2.5 hr. After precipitation into methanol, the polymer (21.5% yield) had $\bar{M}_n$ = 190,000 (membrane osmometry, THF) and T_g = 347K (D.S.C). The homopolymer is not soluble in toluene but is soluble in benzene and THF).

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