Polyelectrolytes with $l\kappa$ = O(1). According to ref 1, the polyelectrolyte is virtually a rigid rod because the persistence length is given by:

$$L_T = \frac{QN^2}{72\xi^2} + L_p \qquad (14)$$

Conclusions

If the Debye–Hückel screening length is well defined by equations (7) and (12), a versatile picture presents itself of polyelectrolyte behaviour at any salt concentration. Incorporated in a consistent manner are: counterion condensation; excluded-volume effects; enlargement of the total persistence length up to and beyond the contour length.

Some remaining problems may be mentioned: (a) a rigorous derivation of the Debye–Hückel potential of mean force for all concentrations of added salt; (b) deviations from Manning's limiting laws when L_p is not large enough to ensure $L_T\kappa \gg 1$[14]; (c) calculation of L_e to second order; generalization for non-wormlike chains; (d) polyion–polyion interactions[13]; a rigorous derivation of the excluded volume, perhaps including dispersion forces caused by fluctuations in the counterion atmosphere of the polyelectrolyte; (e) possible role of short range forces of non-Coulombic origin.

Acknowledgement

The author thanks Professor G. Weill for sending him a preprint of his paper on the persistence length of DNA.

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(Received 24 January 1978)

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Decomposition of benzoyl peroxide in the presence of poly(*N*-vinyl carbazole), poly(*p*-methoxystyrene) and some model compounds

Benzoyl peroxide (BPO) is effective for initiating the polymerization of *N*-vinyl carbazole (VCZ) at 60°C but the reaction does not have the characteristics of a radical process; it appears that initiation results from interaction between the monomer and the initiator[1–3]. The corresponding polymerization of *p*-methoxystyrene (MOS) also shows special features[4]; they are explicable in terms of pronounced transfer to BPO, a process properly regarded as induced decomposition of the initiator. It is relevant that tertiary amine groups are present in VCZ and its polymer, and ether groups in MOS and its polymer; these groups are known to have substantial effects upon the decomposition of BPO[5]. An examination was therefore made of the decomposition of BPO in the presence of polyVCZ, polyMOS, *N*-ethyl carbazole (ECZ) or *p*-ethyl anisole (EAN); ECZ and EAN can be taken as model compounds for the polymers. The samples of polymers had been prepared by radical polymerization in benzene solution using azoisobutyronitrile as initiator.

BPO labelled in its carbonyl groups with ^{14}C was used at a concentration of 0.5 g/dm^3 in benzene. Reaction mixtures were degassed and kept for various periods at 60°C before isotope dilution analysis for carbon dioxide and, in some cases, benzoic acid[6]. *Figure 1* shows that ECZ suppressed the formation of carbon dioxide but the decrease in yield was matched by an increase in that of benzoic acid. It should be noted that the apparent yields of the acid may include contributions corresponding to other substances readily exchanging C_6H_5COO with the acid. *Figure 2* shows that ECZ and polyVCZ depressed the yield of carbon dioxide and markedly reduced $t_{1/2}$ for decomposition of the peroxide. EAN produced effects similar to those produced by ECZ. The influence of polyMOS was much smaller than those of either the model compound EAN or polyVCZ. *Figure 2* shows also that polystyrene and poly(methyl methacrylate) produced no significant effects upon the rate of decomposition of BPO in benzene or upon the yields of carbon dioxide.

Gel permeation chromatography was used to examine polyVCZ for changes caused by treatment with BPO in solution. Chloroform was used as eluent and narrow-distribution samples of polystyrene as standards. For estimation of $\bar{M}_n$ and $\bar{M}_w$, the Q-factor method was applied with values of 41 and 76 for Q for polystyrene and polyVCZ, respectively[7]. The values of molecular weights for samples of VCZ are not exact and are used for comparative purposes only. *Table 1* shows that $\bar{M}_n$ passed through a minimum during the treatment and that $\bar{M}_w$ increased markedly, apparently towards a limiting value; appreciable changes occurred even after decomposition of the peroxide was virtually complete according to results shown in *Figure 2*. Labelled

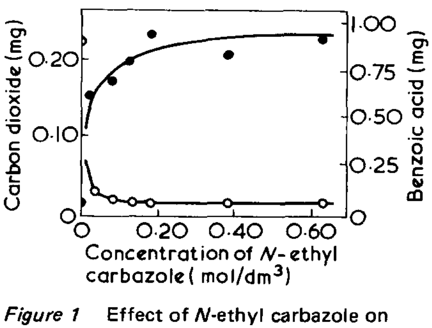

Figure 1 Effect of *N*-ethyl carbazole on products of the decomposition at 60°C for 120 h of 1 mg of benzoyl peroxide in 2 cm^3 benzene: ○, carbon dioxide; ●, benzoic acid

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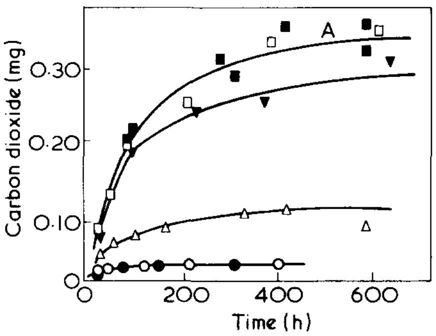

Figure 2 Effects of additives on the production of carbon dioxide during the decomposition at 60°C of l mg of benzoyl peroxide in 2 cm^3 benzene: ●, *p*-ethyl anisole (0.25M); ○, *N*-ethyl carbazole (0.26M); △, poly(*N*-vinyl carbazole) (0.102M in monomer units); ▼, poly(*p*-methoxystyrene) (0.106M in monomer units); □, poly(methyl methacrylate) (0.102M in monomer units); ■, polystyrene (0.102M in monomer units). Line A: pure benzene[6]

groups became attached to polyVCZ in the early stages of the treatment of the polymer with ^{14}C–BPO; it is likely that these groups are responsible for the subsequent changes in the polymer. There were only small changes in $\bar{M}_n$ and $\bar{M}_w$ when solutions of polyVCZ in pure benzene or in benzene containing azoisobutyronitrile were kept at 60°C for periods up to 600 h. It has been shown[8] that, during the thermal degradation of polyVCZ, the distribution of molecular weights broadens probably because of the formation of branched polymers.

The significance of the results presented here will be discussed in a subsequent publication concerned with the polymerizations of VCZ and MOS initiated by BPO.

Table 1 Effects upon poly(*N*-vinyl carbazole) of treatment at 60°C with benzoyl peroxide in benzene

Time (h)	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_w/\bar{M}_n$
0	36.4	286.1	7.86
24	36.8	250.1	6.80
96	33.5	564.4	16.85
329	22.9	1207.7	52.74
600	52.3	1263.0	24.15

Concentration of polyVCZ = 0.102M in terms of monomer units; initial concentration of BPO = 0.5 g/dm^3

Acknowledgements

The experimental work was performed while C.J.D. and J.L. held Research Studentships awarded by the Science Research Council.

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Editorial Announcement

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As a result from January 1979, POLYMER will no longer feature papers on biopolymers or biological macromolecules. Authors, who would normally submit papers in this field to POLYMER are invited to submit their papers to INTERNATIONAL JOURNAL OF BIOLOGICAL MACROMOLECULES. Authors can expect the same high scientific, editorial and production standards set by POLYMER.

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The new journal will publish original research papers and short communications (up to 3000 words) on all aspects of the structure, properties and function of biological macromolecules and their assemblies.