JOURNAL OF
Materials
CHEMISTRY

Suspension cross-linking of poly(aryl ether ketone)s containing carboxylic acid functionality

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Received 30th August 2000, Accepted 1st December 2000
First published as an Advance Article on the web 23rd January 2001

The poly(Friedel–Crafts) reaction between benzene-1,2,4,5-tetracarboxylic dianhydride and diphenyl ether gave carboxylic acid functional polyarylates (PEKK-COOH) that were soluble in polar solvents such as NMP and DMF. The carboxylic acid functional polymers were thermally stable up to 400 °C. PEKK-COOHs in DMF or NMP solution, dispersed in paraffin oil, were cross-linked by reaction of the pendant carboxylic groups with bisphenol-A diglycidyl ether. Insoluble networks were formed by reaction of between 45 and 95 mol% of the carboxylic acid groups. Although regular particles were formed initially, upon drying they formed irregular particulate aggregates that could not be redispersed back to the primary particles. The networks showed a degradative weight loss around 150 °C, which was caused by dehydration from the 2-hydroxypropyloxy group. Further curing of the particles at 160 °C produced a material which did not show any obvious differences in colour or form from the non-heated particles.

Introduction

Polyaromatics are well-established high performance materials originally developed for the aerospace industry. The commercially available materials are typically stable up to temperatures of 500 °C and they have good chemical and radiation resistance but they are difficult to process at moderate temperatures.[1] Although the non-functionalised materials have many uses modification may be desirable for several potential applications (*e.g.* high temperature or radiation resistant filtration membranes). Also, cross-linking of these materials can offer new improved properties such as increased solvent resistance. Two methods of functionalization leading to chain-pendant functionality have been reported: post-polymerization modification and copolymerization with functional monomers. Of these, the most popular is modification after polymerization, which is generally achieved through sulfonation.[2,3,4] Sulfonated polysulfones are, for example, used as separation membranes.[5] Post-polymerization modification has also been used to prepare cyanated polysulfones[6] and carboxylic acid functional polyarylates.[7] On the other hand, the copolymerization route can be used to introduce carboxylic acids,[7] amines[8] and phosphines.[9] Another functionalization method involves the use of polymerization techniques that produce pendant functionality as an intrinsic feature of the synthesis. For example, a feature of the anhydride variant of Friedel–Crafts acylation is that, as well as the acylated aromatic product, the reaction produces carboxylic acids. In the case of the use of a cyclic anhydride the carboxylic acid groups are attached to the newly synthesised material.

Poly(aryl ether ketone)s, such as PEKK [poly(ether ketone ketone)], may be prepared by either a nucleophilic substitution route[10,11] or a poly(Friedel–Crafts) reaction.[12,13] and the anhydride variant of this latter process produces PEKK with pendant carboxylic acid functionality (PEKK-COOH). The PEKK-COOH materials have two carboxylic acid pendants per repeat unit both of which are available for further modifications as dictated by particular applications. They may, for example, be reacted with cross-linking agents to produce networks. One example of a cross-linking strategy could involve the reaction of PEKK-COOH with epoxide functional species such as, the commercially available aryl epoxide, bisphenol-A diglycidyl ether.† The cross-linking process could take several forms but in this report we show how the cross-linking of PEKK-COOH can be used to produce polyaromatic particulates. As far as we are aware no work on the production of PEKK particulates by suspension cross-linking processes has been reported. However, Dosiere *et al.* has previously carried out the Friedel–Crafts reaction, using the diacid chloride procedure, in a precipitation polymerization and reported that their process produces fine dispersions of high molecular weight polymer particles.[14,15] Similar precipitation processes have also been reported to produce needle-like whiskers[16] and fine powders.[17]

Experimental

Synthesis of PEKK-COOH

A typical procedure. A 1 L round-bottomed flask equipped with an overhead stirrer was charged with benzene-1,2,4,5-tetracarboxylic dianhydride (97%, Lancaster Synthesis, 21.81 g, 0.100 mol calculated to include the free acid), aluminium chloride (60.00 g, 0.451 mol) and dry dichloroethane (300 cm^3). To the reaction mixture was added, over a period of ½ h with stirring, a solution of diphenyl ether (99%, Lancaster Synthesis, 18.72 g, 0.110 mol) in dichloroethane (50 cm^3). The mixture was stirred for 72 h at room temperature under a N_2 atmosphere. The reaction was quenched by the careful addition of a 4 : 1 methanol : water mixture (500 cm^3). Once the reactants were fully dissolved conc. HCl (100 cm^3) was added. This resulted in the precipitation of a viscous material, which was collected by decanting off the supernatant liquid. The product was then dissolved in DMF, filtered and reprecipitated into water to give PEKK-COOH (**1**–**7**) as off-white solids. The reaction was repeated using several different stoichiometries, as outlined in Table 1, of benzene-1,2,4,5-tetracarboxylic dianhydride and diphenyl ether.

IR (KBr): 3300, 1725, 1675, 1600 cm^{-1}; ^1H NMR (1 : 1

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†The IUPAC name for bisphenol-A diglycidyl ether is 4,4′-isopropylidenediphenol diglycidyl ether.

DOI: 10.1039/b007052l

$CDCl_3$: TFA): 6–8.5 ppm (m); ^{13}C NMR (1 : 1 $CDCl_3$: TFA): i 199.0, 169.2, 165.3, 143.1, 133.3, 130.4, 129.2, 120.9 ppm; Elemental analysis: found C-71.8%, H-4.0%, N-0.0%; expected C-70.96%, H-3.23%, N-0.00%.

Suspension cross-linking

A 500 cm^3 parallel sided fluted reaction vessel equipped with an overhead-stirrer was charged with a solution of PEKK-COOH (5.00 g), bisphenol-A diglycidyl ether (Lancaster Synthesis, 4.70 g) and Bu_4NBr (0.50 g), as a catalyst, in either NMP or DMF (50 cm^3). Paraffin oil (400 cm^3) was then added with stirring. The mixture was stirred at 150 rpm and heated to 80 °C for 24 h. The particles were recovered by filtration and washed with hexane and then dichloromethane.

MAS NMR ^1H NMR: 6–8.5 ppm (m); ^{13}C NMR: δ 199.0, 169.2, 165.3, 143.1, 133.3, 130.4, 129.2, 120.9 ppm; IR 3500, 1720, 1670 cm^{-1}.

Analysis

MAS NMR was carried out by the EPSRC service at the University of Durham, UK. ^1H and ^{13}C NMR solution spectra were recorded on a JEOL GSX 400 MHz spectrometer using D_6-DMSO as the solvent. SEC (size exclusion chromatography) analysis was performed either in DMF against a polyethylene glycol calibration or in THF with a polystyrene calibration. The chromatograph consisted of three mixed gel 5 μm PlGel, high molecular weight columns connected to refractive index and UV detectors. The flow rate was 1 cm^{-3} min^{-1} and the sample concentration was 2 mg cm^{-3}. SEM micrographs were produced on a JEOL 840A instrument. The samples were prepared on aluminium studs and were gold coated before examination.

Results and discussion

PEKK-COOH

The polymerization is outlined in Scheme 1. Surprisingly little appears to have been reported in the primary literature on the anhydride variant of the poly(Friedel–Crafts) synthesis. In this work we studied the condensation of diphenyl ether and benzene-1,2,4,5-tetracarboxylic dianhydride.

The anhydride route proceeds to high conversion at 20 °C over 72 hours and yields polymers with aromatic carboxylic acid groups, **1**–**7**. Typical NMR spectra are shown in Fig. 1. The key resonance of note from these spectra is at 169.2 ppm in the ^{13}C spectrum, which is assigned to the carbon of the aryl carboxylic acid groups.

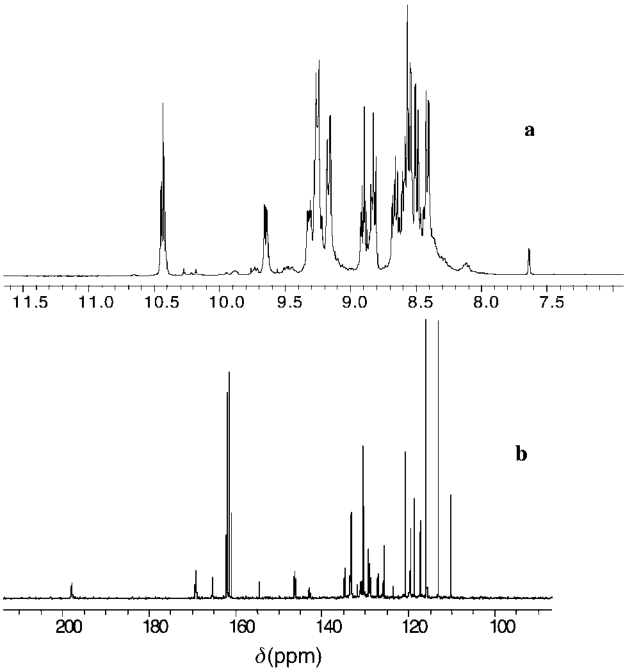


Fig. 1 (a) ^1H and (b) ^{13}C NMR spectra of PEKK-COOH.

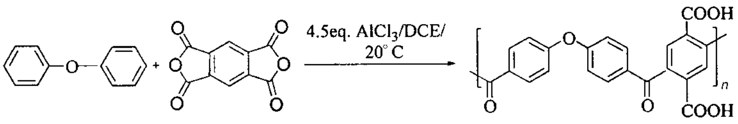
The results of these polymerizations are given in Table 1. The theoretical values for M_n refer to the M_n calculated using the Caruthers equation.

The polymers were soluble in polar solvents such as DMF. Attempts were then made to determine the molecular weight distributions using SEC. However, the rigid nature of these materials produced values of M_n (reported here in poly(ethylene oxide) equivalents) that were unfeasibly high. Also, the PEKK-COOHs **1** to **3** eluted beyond the exclusion limits of any available SEC columns. Not withstanding these comments the results do illustrate the expected trend, that is, lower apparent molecular weights were obtained when the excess of either component was increased.

Interestingly, the two polymerizations containing excess of diphenyl ether gave lower apparent M_n than when excess of dianhydride was used. In order to further investigate this phenomenon propyl ester derivatives of the PEKK-COOH-**6** and PEKK-COOH-**7** were prepared. SEC analysis, using THF as the eluant, gave polystyrene equivalent M_n of 1 900 g mol^{-1} and 2 400 g mol^{-1}, which implied that the SEC of these modified materials did not indicate a significant difference in the size of the two materials prepared using either an excess of

Table 1 Synthesis of PEKK-COOH

	Stoichiometric ratios			M_n /g mol^{-1}		
PEKK	Ph_2O	Dianhydride	$AlCl_3$	Theory	SEC M_n	Yield (wt.%)
1	1.000	1.000	4.5	∞	—	79.7
2	1.0000	1.0251	4.5	31304	—	87.2
3	1.0250	1.0000	4.5	31428	—	89.9
4	1.0000	1.0501	4.5	15604	6 078 000	76.7
5	1.0496	1.0000	4.5	16033	3 903 000	78.2
6	1.0000	1.0998	4.5	8163	3 174 000	43.0
7	1.1031	1.0000	4.5	7915	1 581 000	51.3



Scheme 1 Synthesis of PEKK-COOH.

diphenyl ether or dianhydride. The large difference in apparent M_n obtained following SEC analysis of PEKK-COOH was probably attributed to differences in solution behaviour of these rigid polar polymers rather than true chain size differences. The propylated oligomers were also soluble in THF: a non-solvent for the PEKK-COOHs.

Next the thermal stability of these materials was explored using thermal gravimetric analysis. The polymers showed less than 5% weight loss up to 400 °C. Therefore, these carboxylic acid functional materials display thermal stability that is similar to the analogous non-functional polymers. This result suggests that the presence of the carboxylic acid functionality does not modify the thermal stability of these materials.

Suspension cross-linking

PEKK-COOH prepared from stoichiometries of 1 : 1 had solubilities that were suitable for the suspension cross-linking step. These polymers were soluble in polar solvents such as DMF or NMP and these solutions could be dispersed in paraffin oil without mixing of the paraffin and polar solvent phases. The PEKK-COOHs were cross-linked with bisphenol-A diglycidyl ether. The reaction involved dissolution of a PEEK-COOH and the dispersion of this solution in paraffin oil with controlled agitation. On addition of the diglycidyl ether, reaction between the epoxide groups and a fraction of the pendant carboxylic acid groups produced a cross-linked network, as shown in Scheme 2. Production of chemically functional particles relies on the fact that the PEKK-COOH are highly functional that is they contain two functional groups (COOH) per repeat unit plus the end groups. Formulations that gave rise to particulate dispersions are given in Table 2. Yields of particulate material ranged from 38–73 wt%. It was also possible to leave a substantial proportion of the carboxylic acid sites unreacted but still produce an insoluble network (Table 2, entry 2). Average particle sizes were determined by the sieving procedure. Each polymerization produced distributions of particle sizes and an example of the cumulative distribution of particle sizes obtained using sieving is shown in Fig. 2.

All of the particles were produced initially as regular beads. However, following removal of the solvent the particles coalesced into irregular agglomerated particles.

SEM examination of these materials (exemplified in Figs. 3 and 4) clearly show that the primary particles within the agglomerates were almost spherical and regular. The surface of the particles, examined at a magnification of ×100 and exemplified in Fig. 4, was shown to be relatively featureless and indicated that the particles did not contain macropores.

Table 2 Results of the suspension cross-linking of PEKK-COOH

	PEKK-COOH / g	Solvent	Bisphenol-A diglycidyl ether (g/%^{a})	Weight average^b Particle size /μm	Yield of particles (wt.%)
1	5.00	DMF	4.38/95	620	63
2	5.00	NMP	1.99/45	810	38
3	5.00	NMP	4.38/95	570	71

^{a}Percentage of carboxylic acid groups which would be consumed upon 100% conversion of the diglycidyl ether groups. ^{b}Average diameters were determined by sieving.

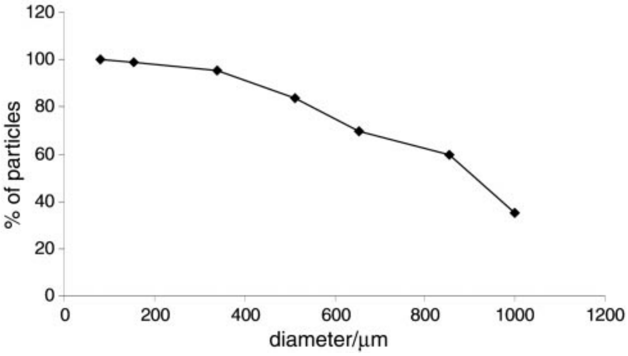


Fig. 2 Cumulative weight distributions of particle diameters greater than the stated diameter.

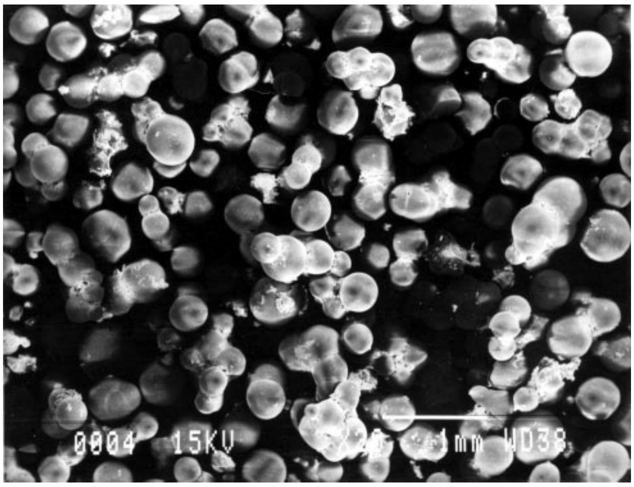
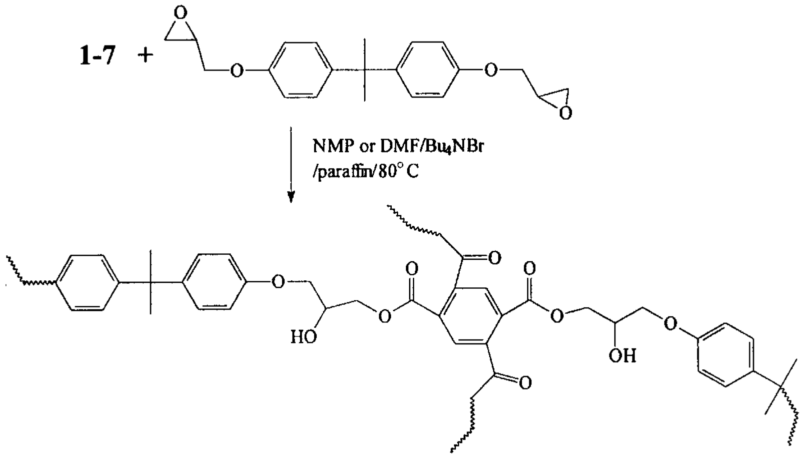


Fig. 3 SEM of a sample of particles (entry 1 in Table 2) at ×20 magnification.



Scheme 2 The network-forming cross-linking reaction.

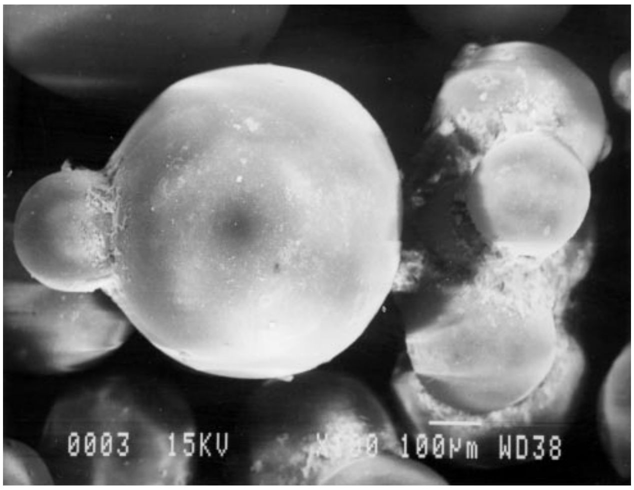


Fig. 4 SEM of a sample of particles (entry 1 in Table 2) at ×100 magnification.

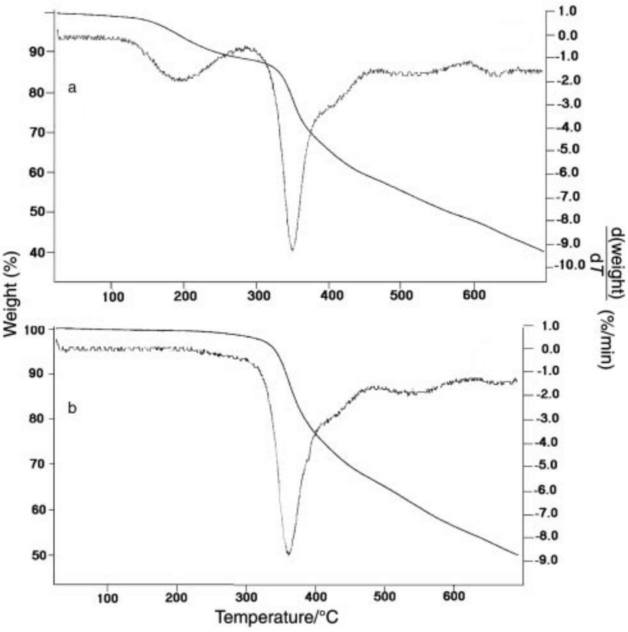


Fig. 5 (a) TGA of beads before curing and (b) after curing.

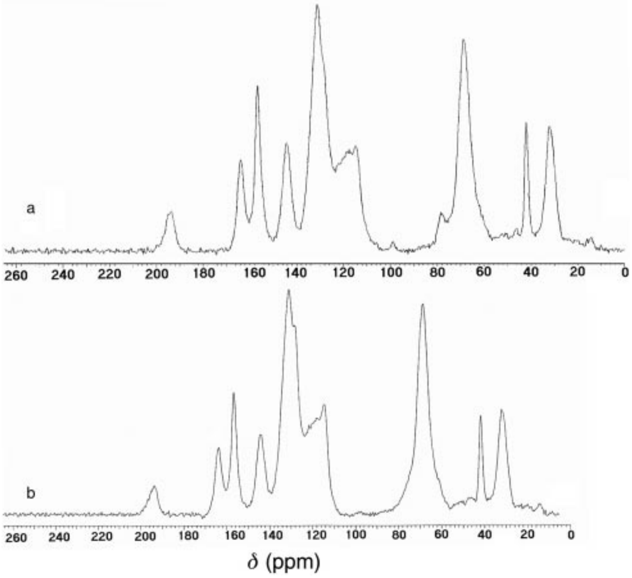


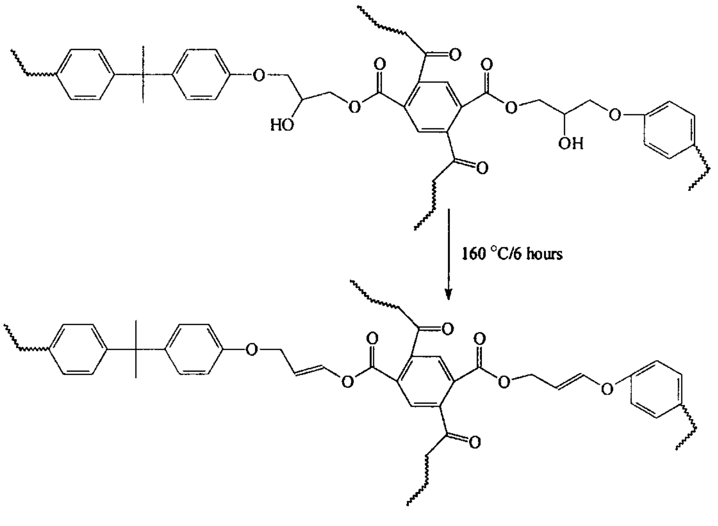
Fig. 6 MAS ^{13}C NMR of the cross-linked material, (a) before heating and (b) after heating (at 160 °C for 6 hours).

Further reactions following thermal treatment

The thermal stability of the new materials was examined using thermal gravimetric analysis (TGA), which showed the polymers are thermally stable up to approximately 320 °C (Fig. 5(a) and (b)). Unlike the previously reported polyimide materials[18] the cross-linked-PEKK materials showed a weight loss at 150 °C (20 wt%). At 320 °C a weight loss of a further 30% was observed. Thus, these particulate materials are less thermally stable than the precursor PEKK-COOH materials.

The instability was probably due to the presence of the 2-hydroxypropyloxy group, which arises from the epoxide–carboxylic acid cross-linking reaction. In order to investigate the thermal stability of these materials a sample of the particles was heated at 160 °C for 6 hours. The TGA of these beads (Fig. 5(b)) showed an absence of the weight loss at 150 °C. A rationale for these curing processes, involving dehydration of the 2-hydroxypropyloxy group, is outlined in Scheme 3.

MAS NMR ^{13}C spectra of the non-heated and heat treated materials are shown in Figs. 6(a) and (b). The main observation to be made from these spectra is that the resonance due to the methine hydroxy group (δ 78.4) produced during the cross-linking epoxide–carboxylic acid reaction is no longer present in the heat treated material. This result implies that heat



Scheme 3 Dehydration following heating at 160 °C.

treatment at 160 °C results in dehydration as proposed in Scheme 3. Unfortunately it was not possible to identify the alkene group that would result from such a reaction. However, TGA analysis of the heat-treated material (Fig. 5(b)) showed that it was thermally stable up to 320 °C and visual examination of the beads showed that they were identical in form and colour to the non-heated beads.

Differences in swelling behaviour were also observed so that the heat-treated material did not swell appreciably in either DMF or chloroform.

Conclusion

We have shown that it is possible to prepare polyarylate networks by suspension cross-linking of carboxylic acid functional polymers formed by the poly(Friedel–Crafts) reaction of an aryl dianhydride and diphenyl ether. Many cross-linking reactions are possible but in this work we have examined the principle of this new dispersion network forming reaction by using the reaction of the diepoxide of bisphenol-A with the pendant carboxylic groups in the absence of dispersants. The particles were insoluble in all common solvents but they swell in solvents like chloroform, DMF and NMP. However, further heat treatment at 160 °C yielded particles that did not swell significantly in any commonly available solvent and they were thermally stable up to approximately 320 °C.

Acknowledgements

We are grateful to the EPSRC solid-state NMR service at Durham University for providing the MAS NMR data and to Dr Nigel Fullwood, Biological Sciences, University of Lancaster, for assistance with the SEM work. Also, acknowledgement is due to EPSRC and BP Amoco Chemicals for providing funds for fellowships for RH and PT (EPSRC grant GR/L39285).

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