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Ultrasonically enhanced persulfate oxidation of polyethylene surfaces

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The ultrasonically enhanced oxidation of polyethylene surfaces by potassium and ammonium persulfates is described. The use of ultrasound allows significant levels of surface modification to be achieved using these oxidizing agents under mild conditions. Changes in the water contact angle and attenuated total reflection infra-red spectra were used to follow the changes in surface chemistry. Variation of conditions such as sonication time, sound intensity and reaction temperature allowed control over the extent and nature of the surface oxidation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: surface modification; polyethylene oxidation; high intensity ultrasound; sonochemistry)

INTRODUCTION

Polyolefins, including polyethylene, are commonly used for a wide range of applications. They are usually considered to be stable and inert, while being relatively inexpensive. However, their inert nature leads to low surface energies and consequent problems of adhesion of coatings as well as to other materials[1,2]. There is thus great interest in modifying the chemical functionality of the surface to make it more receptive to other components including improving biocompatibility.

A number of methods have been developed for modifying polyethylene surfaces[3,4]. Free radical chlorination[5,6] and sulfonation[7] have been used to introduce functionality, but most methods rely on oxidation to introduce the polar groups to the surface which raises the surface energy and hence promotes adhesion etc. Techniques[3] for achieving this include corona and plasma discharges, photooxidation, ozonation as well as chemical reaction. The most commonly used chemical oxidant is chromic acid[8]. Blais *et al.*[9] showed that hydroxyl groups and several different types of carbonyl functions were introduced at the surface while Rasmussen *et al.* suggested that the main product was carboxylic acid functionality[10]. Clearly, the large scale use of chromic acid is undesirable and it would be more convenient to employ a milder, more 'environmentally-friendly' oxidizing agent.

Metal persulfates are well known[11] sources of radicals in aqueous solution, for example in the initiation of polymerization. The mechanism of the thermal decomposition is believed[12] to involve the sulfate radical which can abstract a hydrogen from water to give hydroxyl radicals:

$$S_2O_8^{2-} \rightarrow 2\,SO_4^{-\bullet}$$

$$2\,SO_4^{-\bullet} + H_2O \rightarrow HSO_4^{-} + HO^{\bullet}$$

Either of the radical species can remove a hydrogen from the PE surface after which hydroxylation can occur to give an oxidized surface. In a recent report[13] Bamford and Al-Lamee described the persulfate oxidation of the surfaces of several polymers.

Over the past two decades, the use of high intensity ultrasound has become a common technique in synthetic chemistry[14–16]. A number of reactions, especially those in heterogeneous systems, have been shown to give enhanced rates and yields under ultrasound, leading to a branch of chemistry sometimes termed *sonochemistry*. The best known effect in polymer sonochemistry is the cleavage of chains when irradiated in solution[17,18], although more recently ultrasound has been applied to polymer synthesis with some success[19].

The main effects of sonication are due to *cavitation* or the nucleation, growth and explosive collapse of microscopic bubbles on a microsecond timescale[20]. This can result in the formation of relatively high concentrations of excited species such as radicals which can be used to initiate reactions[21]. Motion of the solvent molecules around bubbles causes very efficient mixing and dispersion of multi-phase systems. An extra effect occurs near a solid surface when cavitational collapse is asymmetric[22,23] and results in a microjet of solvent and dissolved reagents impinging at high speed on the solid[24], which increases the rate of transfer of reactants and products to and from the surface.

Urban and Salazar-Rojas[25] utilized these effects to

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Table 1 Water contact angles for persulfate[a] treated PE surfaces

Reagents	Conditions	Water contact angle (°)	
		Ultrasound	Control
Water	Air, 35°C	94	97
$K_2S_2O_8$	Air, 35°C, 33 g dm^{-3}	82	96
$K_2S_2O_8$	N_2, 35°C, 33 g dm^{-3}	84	99
$K_2S_2O_8$	Air, 75°C, 33 g dm^{-3}		95
$K_2S_2O_8$	Air, 35°C, 33 g dm^{-3} + 0.5 g dm^{-3} sodium metabisulfite	90	
$K_2S_2O_8$	Air, 35°C, 33 g dm^{-3} + 2.0 g dm^{-3} iron (III) chloride	82	
$K_2S_2O_8$	Air, 35°C, 33 g dm^{-3} in 0.05 mol dm^{-3} sodium hydroxide	93	
$K_2S_2O_8$	Air, 35°C, 33 g dm^{-3} in 0.05 mol dm^{-3} sulfuric acid	89	
$(NH_4)_2S_2O_8$	N_2, 35°C, 33 g dm^{-3}	92	98

[a] All reaction times were 5 h. Sonication intensity was 26.2 W cm^{-2}

remove HF from the surface of poly(vinylidene difluoride) (PVF_2), to give extended conjugation. The conventional approach is to treat the polymer with a hot solution of a strong base together with a phase transfer catalyst. The use of ultrasound accelerated the dehydrofluorination, particularly at low temperatures. The unsaturation gives sites which can be further modified by subsequent chemical reaction. Examples[26,27] of this have been seen with the grafting of silicon and germanium centred phthalocyanines onto the surface of PVF_2.

There are two main effects of ultrasound which could be beneficial in promoting the oxidation at polymer surfaces. Firstly, the production of radicals could be accelerated by enhanced decomposition of persulfate salt. In an early report, Schumb and Ritner[28] showed that the rate of decomposition of potassium persulfate was slightly increased during sonication at 8.7 kHz. More recently, Lorimer *et al.*[29] reported an increase in the rate of decomposition, although only temperatures between 50 and 70°C were used. Related work by the authors[30] has shown that the rate of radical formation in this system is accelerated threefold at 55°C, but by a factor of ten at 35°C. In addition, the enhanced mass and phase transfer properties around solid surfaces caused by ultrasound could enhance the oxidations.

It would clearly be of considerable interest if PE surfaces could be oxidized by systems less problematic than chromic acid or a plasma discharge. A number of systems were studied and these are described in detail elsewhere[31], but this paper will describe the use of persulfates as oxidizing agents.

EXPERIMENTAL

Materials

Polyethylene (PE) was a commercial, LDPE sample with a weight average molecular weight of 145 000 and polydispersity of 7.0, and was melt pressed into sheets of thickness 0.2–0.3 mm. All reagents and solvents were of the purest grade available from Aldrich Ltd.

Sonication procedures

Samples of the PE sheets were cleaned by swabbing with methanol and dichloromethane followed by drying in a stream of dry air. They were clamped in a steel holder immersed in approximately 150 cm^3 of the appropriate reagent solution contained in a jacketted beaker. Thermostatted water was circulated to maintain temperature at ±0.5–1.0°C depending on the starting temperature. Except where noted, experiments were carried out at 35°C since cavitation in water is maximized at this temperature[32]. A 'Sonics and Materials' VC600 ultrasound horn system was fitted so that the horn tip was 3 cm above the PE film. The intensity of ultrasound, measured calorimetrically[33] was 26.2 ± 1.5 W cm^{-2}. Blank experiments were carried out in the same apparatus without switching on the ultrasound but with magnetic stirring. After treatment, the films were rinsed with clean water and acetone before being dried under vacuum.

Polymer analysis

Infra-red (i.r.) spectra were recorded on a Nicolet 510P spectrometer with a variable-angle attenuated total reflectance (ATR) accessory utilizing a KRS-5 prism. Spectra were measured with a resolution of 4 cm^{-1} by averaging 150 scans. Contact angles were measured on a home-built apparatus using water purified by ion-exchange. The treated PE films were clamped horizontally on a steel base inside a perspex box, the inside of which was maintained at a relatively constant, high humidity. Droplets of 10 ± 1 μl were placed on the film from a microsyringe and observed through a travelling microscope fitted with a goniometer eye-piece. All measurements were made at 21 ± 1.5°C and were the average of at least ten readings at different positions across the surface. The uncertainty in the values was at most ±5°. In most cases, measurements were performed shortly after treatment while for other experiments, measurement was delayed for up to 12 h. No significant differences in the measured values were noted for these cases.

RESULTS AND DISCUSSION

The contact angle of water on the untreated PE films was 98.6 ± 2.5°. As noted above, one of the more common methods for oxidizing PE is the use of chromic acid which results in contact angles of 45–66° [9,34]. Treatment of the PE used here with chromic acid according to the method of Rasmussen *et al.*[10] yielded

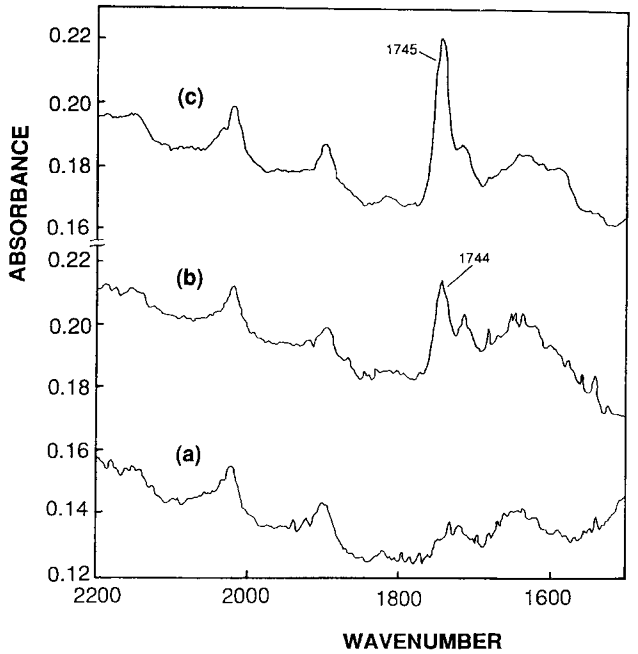

Figure 1 ATR i.r. (60°) spectra of PE surfaces: (a) control reaction; (b) reacted with $K_2S_2O_8$ at 75°C; (c) $(NH_4)_2S_2O_8$ at 35°C with ultrasound

films with contact angles of 60 ± 2.5°, in agreement with literature values[10].

In this initial work, a preliminary survey was undertaken of the potential for the ultrasonic oxidation of PE films of aqueous potassium and ammonium persulfate solutions, along with reagents known to promote the decomposition of persulfate systems. *Table 1* shows the results of treating PE films for 5 h with a range of systems.

It is clear that all of the ultrasonically promoted reactions gave changes in contact angle from the untreated PE larger than the uncertainty of ±5° while none of the stirred, control reactions at the same temperature showed significant changes. These changes cannot be ascribed to either the aqueous environment alone or the increase in surface roughness since sonication in water failed to significantly change the contact angle.

Reaction with potassium persulfate both under air and nitrogen at 35°C gave similar results with a decrease in contact angle of around 16°. The thermal reaction at 75°C would, from other work, yield a similar rate of radical formation as the sonochemical system at 35°C. However, the reduction in contact angle was much lower, indicating that ultrasound is enhancing the reaction at the surface as well as accelerating the production of radical species. Addition of sodium metabisulfite, a known accelerator for persulfate decomposition resulted in less change in the wetting characteristics of the PE than the persulfate alone. Addition of trace amounts of metal ions has also been reported to increase the rate of decomposition of the persulfate system[35]. In this work Fe^{3+} was added to the system, but no further improvement was noted over the use of persulfate alone.

Studies of the thermal decomposition kinetics for sodium and potassium persulfate in basic, neutral and dilute acid solutions by Green and Mason[36], and later by Kolthoff and Miller[37], showed that the reaction is catalysed by the addition of acids. Reactions were therefore carried out in dilute acid and base solutions. Again, the contact angles after treatment were significantly different from the starting PE, but the changes were less than those obtained in neutral media. These results are consistent with the radical mechanism suggested above. Kolthoff and Miller suggested that, in acidic media, the reaction proceeded via HSO_4^- so that the intermediates are ionic. These mechanisms are consistent with sonochemically enhanced reactions since a number of workers have reported that in heterogeneous systems, radical reactions are preferentially accelerated by ultrasound over those proceeding by solely ionic pathways[38,39]. Indeed, it has been observed[40] in some heterogeneous sonochemical reactions that only the single electron transfer pathway operates even where the major product in the absence of ultrasound arises from an ionic mechanism. The contact angle changes in *Table 1* also signify that some reaction occurred with ammonium persulfate, although modification in these terms appeared to be more substantial with the potassium salt.

In an attempt to identify the species responsible for the change in surface chemistry, ATR i.r. spectra were recorded. Unfortunately, at the sensitivity available, no differences could be found between untreated PE films and those which had been sonicated in any of the potassium persulfate solutions. The ATR i.r. spectrum from the reaction carried out by heating to 75°C did however suggest the presence of a carbonyl stretching band at 1744 cm^{-1} as shown in *Figure 1b*. The spectra recorded from the film treated with ammonium persulfate, shown in *Figure 1c* also showed the presence of a new strong absorbance at $\sim$1745 cm^{-1}. The position of this band is consistent with the carbonyl stretching of organic esters.

The difference in the results obtained at different temperatures is likely to be due to the much softer surface and hence increased mobility of polymer chains closer to T_g resulting in deeper penetration of reagents into the film and hence a greater i.r. sampling depth. At 35°C the polymer is much harder and hence functionalization will be more localized at the surface. The contact angle changes and ATR i.r. results are somewhat conflicting, since the former suggest that the potassium salt causes greater oxidation of the surface while the spectra suggest that the ammonium salt causes greater functionalization. These observations can be reconciled by suggesting that a greater level of oxidation is achieved with ammonium persulfate but that the oxidized layer is more diffuse and distributed over a deeper region of the i.r. sampling depth which is in the micrometer range. Oxidation caused by the potassium salt seems to be confined to the outermost molecular layers and so is too small and remains undetected by ATR i.r.

Previously, Morris has studied the effects of ammonium persulfate treatment on polyethylene adhesive joint strengths[41] and found large increases in joint strength using dilute solutions. Although only small changes in the critical surface tension were observed small carbonyl peaks were reported to be visible in the ATR i.r. spectra. Treated samples were also reported to be partially insoluble and the increased adhesive joint strength was

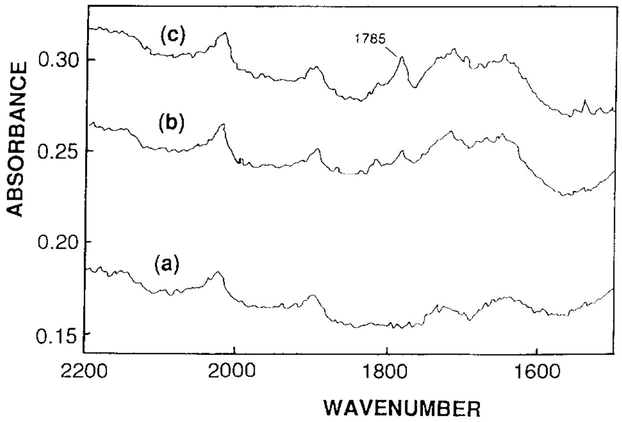

Figure 2 ATR i.r. (60°) spectra of PE surfaces: (a) unreacted PE; (b) PE reacted with TFAA; (c) oxidized with $K_2S_2O_8$ at 35°C with ultrasound then reacted with TFAA

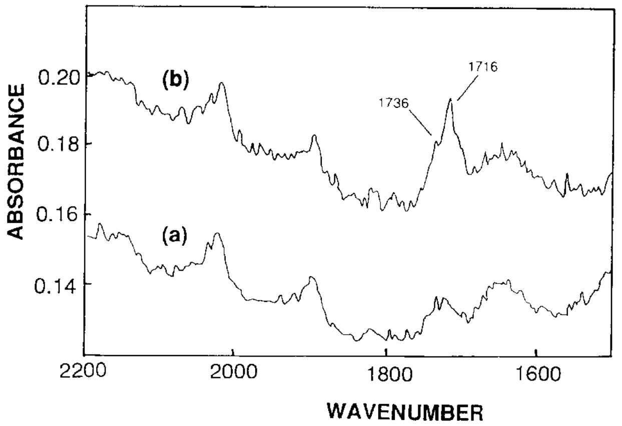

Figure 4 ATR i.r. (60°) spectra of PE surfaces: (a) control reaction; (b) 24 h sonication with $K_2S_2O_8$ at 35°C and 26 W cm^{-2}

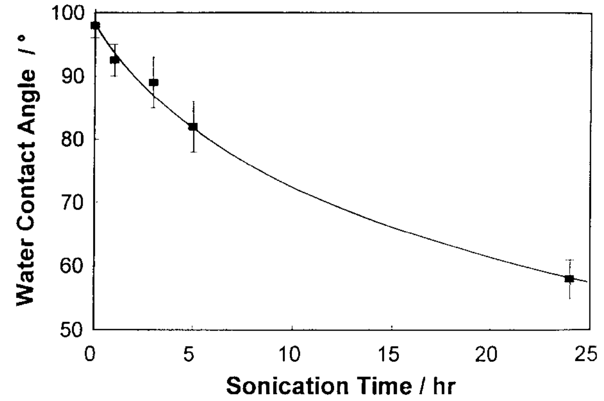

Figure 3 Change in water contact angle of PE surface during sonochemical treatment with $K_2S_2O_8$ at 35°C and 26 W cm^{-2}

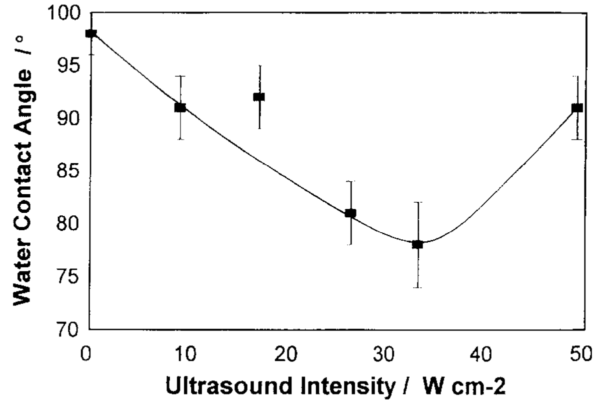

Figure 5 Water contact angle of PE surface after 5 h sonochemical treatment with $K_2S_2O_8$ at varying intensities at 35°C

attributed to surface crosslinking. In our work, no evidence for crosslinking was obtained with any of the films as they remained completely soluble in hot decalin.

An alternative explanation of the absence of spectral information in the potassium persulfate treated films is that the modification produced a highly hydroxylated surface rather than inducing carbonyl functionality. Samples of the PE film oxidized under the conditions above were further reacted with trifluoroacetic anhydride (TFAA) vapour which selectively reacts with hydroxyl and related functionality to form fluoroesters[42]. The ATR i.r. spectra of the original and derivatized PE samples are shown in *Figure 2*. The characteristic fluoroester peak at ~1785 cm^{-1} is clearly present in the oxidized polyethylene sample to a much greater degree than in the untreated PE.

The encouraging initial results of obtaining significant levels of surface oxidation led us to investigate the effect of treatment time and varying the ultrasound intensity in order to maximize the oxidation and to determine the available degree of control over the process. *Figure 3* shows the variation in contact angle with treatment time under the conditions described above. The displayed error bars indicate the variation observed over at least ten measurements across the film. The plot indicates that the extent of oxidation increases markedly with longer treatment times and, after 24 h, reaction equivalent to treatment with chromic acid can be achieved. The ATR i.r. spectrum of the PE film after 24 h sonication is shown in *Figure 4*. The two absorption bands at 1716 cm^{-1} and 1736 cm^{-1} are in positions characteristic of carbonyl functions such as ketone, carboxylic acid and ester groups which could arise from further oxidation of hydroxyl substituents at the surface.

Another way of increasing the reactivity in terms of the number of cavitation bubbles produced is to increase the sound intensity. *Figure 5* shows the results of variation of this for fixed reaction times of 5 h and demonstrates that the extent of oxidation does increase although the effect is relatively small. There is a maximum intensity, in this case 32 W cm^{-2}, above which the benefit of increasing the intensity is lost. This has been noted in a number of sonochemical systems and can be attributed to the intense cavitation field near the horn disrupting passage of sound into the liquid and hence reducing the overall degree of cavitation. It should also be noted that the plot in *Figure 5* mirrors that measured elsewhere[30] for the decomposition of potassium persulfate, suggesting that the rate of oxidation appears to be limited by the number of cavitational events resulting in radical production.

As noted above, there are a number of possible ways in which sonication could enhance the surface oxidation. The first of these is merely to accelerate the decomposition of persulfate and hence production of reactive intermediates. However, rate measurements[30] suggest that this alone is unable to explain the extent of the results described here. The collapse of cavitation bubbles in the vicinity of the PE film will result in microjets of solution impinging on the surface at high speed. In addition to further enhanced mass transfer of reagents, this may cause local heating at the surface and it will definitely result in deformation and chain movement in the outermost layers[43]. It is not known whether these would be sufficient to induce chain breakage but this may also be responsible for enhanced reactivity. These processes are responsible for the cleaning effects of ultrasound and in some cases lead to erosion, particularly for metal surfaces. Under the conditions used here, no significant erosion was noted[43] but this does not preclude effects on a molecular scale.

CONCLUSION

This work has shown that the use of ultrasound allows the oxidation of polyethylene surfaces using persulfate oxidizing agents under mild conditions. The oxidation proceeds initially through the generation of surface hydroxyl groups which can be reacted further to give carboxylic acids and esters on extended reaction. This functionality gives sites where further modification such as grafting can be performed. At long sonication times the oxidation layer gave a similar contact angle to the more conventional chromic acid oxidized samples. Under the conditions used, the process is relatively slow, but equipment is now available to operate at higher power densities and much higher scale. This work further suggests that the degree and nature of the surface functionality could be controlled to some degree by varying the sonication time, sound intensity and reaction temperature.

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REFERENCES

1 Feast, W. J. and Munro, H. S. 'Polymer Surfaces and Interfaces', Chichester, 1987
2 Brewis, D. M. and Briggs, D. *Polymer* 1981, **22**, 7
3 Lane, J. M. and Hourston, D. J. *Prog. Org. Coatings* 1993, **21**, 269
4 Bergbreiter, D. E. *Prog. Polym. Sci.* 1994, **19**, 529
5 Cross, E. M. and McCarthy, T. J. *Macromolecules* 1992, **25**, 2603
6 Puszynski, A. and Godniak, E. *Makromol. Chem. Rapid Commun.* 1980, **1**, 617
7 Olsen, D. A. and Osteraas, A. J. *J. Polym. Sci., Part A* 1969, **7**, 1921
8 Briggs, D. in 'Surface Analysis and Pretreatment of Metals and Plastics' (Ed. D. M. Brewis), Applied Science, New York, 1982
9 Blais, P., Carlsson, D. J., Cullog, G. W. and Wiles, D. M. *J. Colloid Interface Sci.* 1974, **47**, 636
10 Rasmussen, J. R., Stedonski, E. R. and Whitesides, G. M. *J. Am. Chem. Soc.* 1977, **99**, 4736
11 Eastmond, G. C. in 'Comprehensive Chemical Kinetics', Vol.14A (Eds. C. H. Bamford and C. F. H. Tipper), Elsevier, Amsterdam, 1976
12 Bartlett, P. D. and Colman, J. D. *J. Am. Chem. Soc.* 1949, **71**, 1419
13 Bamford, C. H. and Al-Lamee, K. G. *Makromol. Chem. Rapid. Commun.* 1994, **15**, 379
14 Suslick, K. S. 'Ultrasound: Its Chemical, Physical and Biological Effects', V.C.H. Publishers, New York, 1990, Chapter 4
15 Ley, S. V. and Low, C. R. 'Ultrasound in Chemistry', Springer Verlag, London, 1989
16 Price, G. J. (Ed.) 'Current Trends in Sonochemistry', R.S.C. Special Publication 116, R.S.C., Cambridge, 1992
17 Basedow, A. M. and Ebert, K. *Adv. Polym. Sci.* 1977, **22**, 83
18 Price, G. J. *Adv. in Sonochem.* 1990, **1**, 231
19 Price, G. J. in 'New Methods of Polymer Synthesis', Vol. 2, (Eds. J. R. Ebdon and G. C. Eastmond), Blackie (in press)
20 Leighton, T. 'The Acoustic Bubble', Academic Press, London, 1994
21 Price, G. J., Norris, D. J. and West, P. J. *Macromolecules* 1992, **25**, 6447
22 Doktycz, S. and Suslick, K. S. *Science* 1990, **247**, 1067
23 Pugin, B. and Turner, A. T. *Adv. Sonochem.* 1990, **1**, 81
24 Lauterborn, W. and Hentschel, W. *Ultrasonics* 1984, **24**, 59
25 Urban, M. W. and Salazar-Rojas, E. M. *Macromolecules* 1988, **21**, 372
26 Exsted, B. J. and Urban, M. W. *J. Inorg. Organomet. Polym.* 1993, **3**, 105
27 Exsted, B. J. and Urban, M. W. *Polymer* 1994, **35**, 5560
28 Schumb, W. C. and Ritner, E. S. *J. Am. Chem. Soc.* 1940, **62**, 3416
29 Lorimer, J. P., Mason, T. J., Fiddy, K., Groves, R. and Dodgson, D. *Ultrasonics International Conference Proceedings* 1989, 1283
30 Price, G. J. and Clifton, A. A. *Polymer* (in press)
31 Price, G. J. and Clifton, A. A. *Macromolecules* in press
32 Niemczewski, B. *Ultrasonics* 1980, **18**, 107
33 Mason, T. J. 'Practical Sonochemistry', Ellis Horwood, Chichester, 1991
34 Briggs, D., Brewis, D. M. and Konieczko, M. B. *J. Mater. Sci.* 1976, **11**, 1270
35 Samal, R. K., Nayak, M. C. and Das, D. P. *Eur. Polym. J.* 1982, **18**, 313
36 Green, L. and Mason, O. *J. Chem. Soc.* 1970, **97**, 2083
37 Kolthoff, I. M. and Miller, I. K. *J. Am. Chem. Soc.* 1951, **73**, 3055
38 Price, G. J. (Ed.) 'Current Trends in Sonochemistry', R.S.C. Special Publication 116, R.S.C., Cambridge, 1992, p. 34
39 Luche, J. L., Einhorn, C., Einhorn, J. and Sinisterra-Gago, J. V. *Tetrahedron Lett.* 1990, **31**, 4125
40 Ando, T., Bauchat, P., Foucaud, A., Fujita, M., Kimura, T. and Sohmiya, H. *Tetrahedron Lett.* 1991, **32**, 4709
41 Morris, C. E. M. *J. Appl. Polym. Sci.* 1970, **14**, 2171
42 Chilkoti, A. and Ratner, B. D. *Surf. Interface Anal.* 1991, **17**, 567
43 Price, G. J., White, A. M. and Clifton, A. A. *Polymer* 1995, **36**, 4919