JOURNAL OF Materials CHEMISTRY

Electrically conductive graft copolymers of poly(methyl methacrylate) with varying polypyrrole and poly(3-alkylpyrroles) contents

Siu-Choon Ng,[a]* Hardy S. O. Chan[a,b] Jun-Feng Xia[a] and Wanglin Yu[a]

[a] *Department of Chemistry, National University of Singapore, Kent Ridge Crescent, Singapore 119260*

[b] *Department of Materials Science, National University of Singapore, Kent Ridge Crescent, Singapore 119260*

Received 27th April 1998, Accepted 14th August 1998

Pyrrole and 3-alkylpyrroles were grafted *via* chemical oxidative polymerisation with $FeCl_3$ to copolymers of methyl methacrylate and ω-(*N*-pyrrolyl)alkyl methacrylates incorporating varying amounts of ω-(*N*-pyrrolyl)alkyl methacrylates with varying alkyl chain lengths. The electrical conductivity of the resultant graft copolymers attained 10^{-4}–10^{-3} S cm^{-1}, with the length of the alkyl spacers in ω-(*N*-pyrrolyl)alkyl methacrylates having little influence on the conductivity. A longer alkyl spacer, however, resulted in a lower glass transition temperature for the resulting graft copolymers. The graft copolymers from pyrrole were insoluble whilst those arising from 3-alkylpyrroles were completely soluble in common organic solvents even in their doped states.

The past two and a half decades have witnessed intense interdisciplinary research attention on electrically conducting conjugated polymers such as polyacetylenes, polyanilines, polypyrroles and polythiophenes on account of their remarkable electronic, magnetic and optical properties as well as their potential in a wide range of technological applications.[1–6] However, the generally poor processability of these parent unfunctionalised systems has severely limited their applications. Consequently, much research has been devoted to improving the processability of the conductive polymers.[7–12] Amongst these approaches, the combination of conducting polymers, particularly polypyrroles, with conventional polymers has been the recent focus of several research groups. Polypyrrole was first grafted onto polystyrene by electrochemical polymerisation of pyrrole in the presence of a pyrrole derivative of polystyrene.[7] The graft copolymers had electrical conductivity of 0.05–5 S cm^{-1} depending on the pyrrole content. However, no information pertaining to the processability of the graft copolymers was reported. Over the past several years, Stanke and co-workers have successfully grafted polypyrrole to poly(methyl methacrylate) (PMMA) by effecting the chemical oxidative polymerisation of pyrrole in the presence of methyl methacrylate–2-(*N*-pyrrolyl)ethyl methacrylate copolymer using $FeCl_3$ as an oxidant.[12] The film conductivity of the graft copolymers attained a maximum of 2×10^{-2} S cm^{-1},[12a,12c] though only marginal solubility was achieved.[12a] Although soluble samples of the graft copolymers could be obtained at a very low polypyrrole content,[12b] no corresponding conductivity datum was reported. In addition, only an *N*-pyrrolylethyl spacer group on the pendant ester in the precursor copolymer was studied. It is anticipated that incorporation of longer alkyl spacers between pyrrole and the PMMA backbone will have a significant impact on both the electrical conductivity and processability of the resultant graft copolymers. Accordingly, with a view to investigating structure–property relations, we have synthesized a series of graft copolymers of polypyrrole and poly(3-alkylpyrroles) with the copolymers of methyl methacrylate (MMA) and ω-(*N*-pyrrolyl)alkyl methacrylate of different *n*-alkyl chain lengths. It was found that the attachment of long alkyl groups at the 3-position of pyrrole afforded soluble, film-castable graft copolymers in their doped states with electrical conductivity in the semiconducting range.

Experimental

Synthesis of key monomers

Pyrrole (Py), methacryloyl chloride and methyl methacrylate (MMA) were distilled prior to use. α,α′-Azobis(isobutyronitrile) (AIBN) (Koch-Light) was recrystallized from absolute ethanol and dried at 40 °C *in vacuo* (0.2 mmHg). Triethylamine, dimethyl sulfoxide (DMSO) and nitromethane were distilled over CaH_2. Other chemicals were used as received.

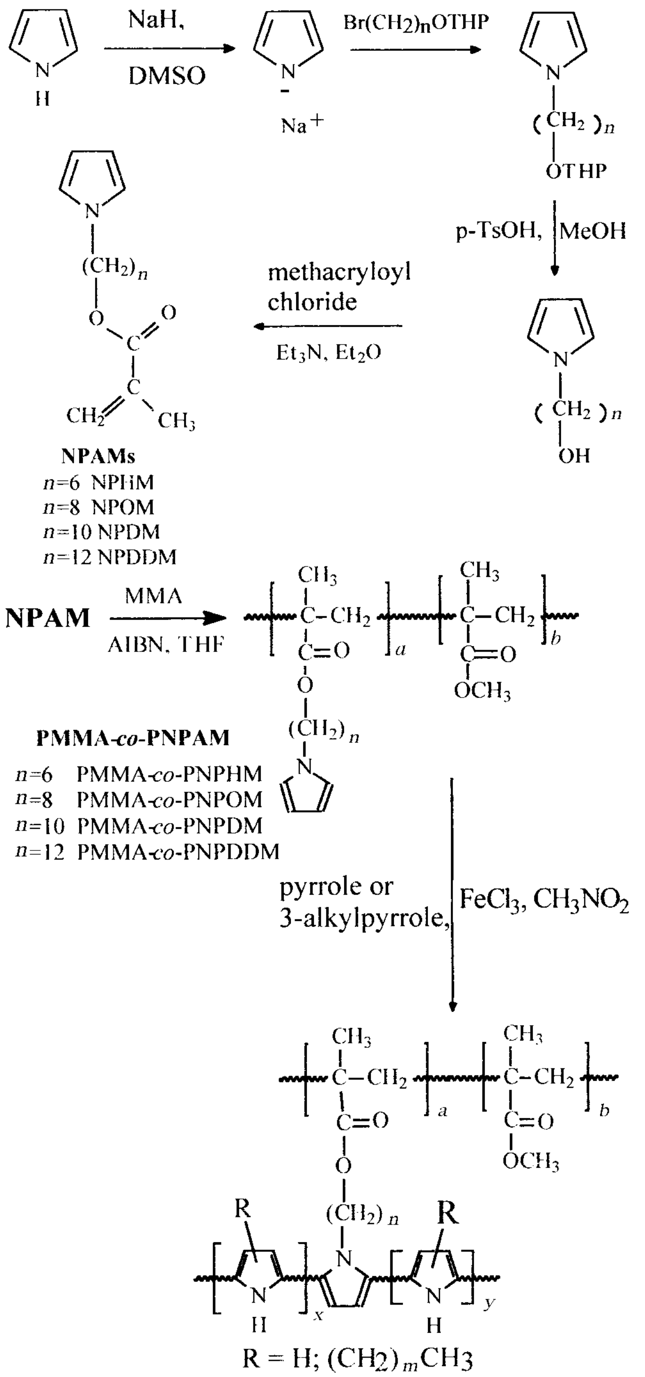
The key monomers of ω-(*N*-pyrrolyl)-*n*-alkyl methacrylate (NPAM) were synthesized as shown in Scheme 1. Tetrahydropyran (THP)-protected ω-bromoalkanols used in this synthesis were prepared by bromination of α,ω-diols[13] followed by THP-protection of the terminal hydroxy groups. 3-Alkylpyrroles (3APys) were synthesized according to literature procedures[14,15] except for the replacement of $LiAlH_4$ for $NaAlH_2(OCH_2CH_2OCH_3)_2$ as the reducing agent.

Polymerization

The graft copolymers, poly[methyl methacrylate-*co*-ω-(*N*-pyrrolyl)alkyl methacrylate]s (PMMA-*co*-PNPAMs): PMMA-*co*-PNPHM, PMMA-*co*-PNPOM, PMMA-*co*-PNPDM, and PMMA-*co*-PNPDDM corresponding to *n*-alkyl spacers of 6, 8, 10 and 12 carbons, respectively, in NPAMs were obtained by copolymerization of methyl methacrylate (MMA) with the corresponding NPAMs in THF at 60 °C for 22 h using AIBN as an initiator. Thereafter, pyrrole and 3-alkylpyrrole moieties were grafted onto PMMA-*co*-PNPAMs by effecting oxidative polymerisation with 2.5 mole equivalents of anhydrous $FeCl_3$ in nitromethane at 0 °C for 6 h (Scheme 1). The resultant graft copolymers were precipitated by pouring into 5% HCl in methanol at 0 °C. The precipitate was washed with methanol until the solvent remained colorless (for the pyrrole grafted copolymers, the precipitate was stirred in THF overnight after washing with methanol)[12b,12e] and dried under vacuum (0.1 mmHg) at room temperature for 24 h.

Measurements

Elemental analyses from which the compositions of the copolymers and the graft copolymers were calculated were performed at the National University of Singapore



Scheme 1 Reaction scheme for the syntheses of key monomers of ω-(*N*-pyrrolyl)-*n*-alkyl methacrylate and graft copolymers with polypyrroles and poly(3-alkylpyrrole)s.

Microanalytical Laboratory on a Perkin Elmer 240C elemental analyzer for C, H and N determinations. FT-IR spectra of polymers dispersed in KBr disks were recorded on a Bio-Rad TFS156 spectrometer. ^{1}H NMR were recorded on a Bruker ACF 300 FT-NMR spectrophotometer operating at 300 MHz. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) as internal reference. Thermogravimetric analyses (TGAs) of polymer powders (about 5 mg) were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer. A heating rate of 10 °C min^{-1} with an air flow of 75 ml min^{-1} was used, the runs being conducted from room temperature to 800 °C. Differential scanning calorimetry (DSC) was conducted with a DSC 2910 module in conjunction with the Du Pont Thermal Analyst system. The analyses were conducted from room temperature to 400 °C at a heating rate of 10 °C min^{-1} with about 3 mg samples. Conductivity measurements were carried out on a four point probe connected to a Keithley constant-current source system. Gel permeation chromatographic analyses were carried out using a Waters 600E HPLC system with a Waters 410 differential refractometer. The molecular weights referred to the peak maxima of the elution curves were measured against polystyrene standards in THF at 30 °C using the following column combination: Phenogel™ MXL and MXM columns (300 mm × 4.6 mm ID), with a separating range from 10^3 to 10^6 g mol^{-1}.

Results

Precursor copolymers PMMA-*co*-PNPAMs

The PMMA-*co*-PNPAM samples prepared in our experiments were soluble white powders with molecular weights (M_n) of *ca.* 50 000 g mol^{-1}. Their chemical structures were confirmed by ^{1}H NMR and FTIR spectroscopy. A representative ^{1}H NMR spectrum for PMMA-*co*-PNPDDM containing 7.7 mol% of pyrrolyl moieties revealed resonances for the α-, β-ring protons at δ 6.65 and 6.13 respectively.[16a,16b] The corresponding FT-IR spectra of the PMMA-*co*-PNPAMs depict characteristic vibrational bands at 1730 cm^{-1} (ascribable to ester carbonyl vibrations), 750 and 725 cm^{-1} ascribable respectively to pyrrole C–H$_\beta$ and C–H$_\alpha$ bendings (Fig. 2a).[12a,12c,12e]

TGA in air for PMMA-*co*-PNPAMs revealed an onset decomposition temperature at 180–240 °C, being completely degraded at *ca.* 450 °C leaving residues of <0.5%. Glass transition temperatures (T_g) of the copolymers were found to be lowered with increasing content of NPAMs. In addition, T_g at a given mole percentage of NPAM in the copolymer was also reduced with increasing length of the *n*-alkyl spacers in NPAMs (see Fig. 1) suggesting enhanced chain mobility of the copolymers with the longer spacers.

Graft copolymers of PMMA with polypyrrole

Black insoluble electrically conductive materials resulted from grafting of polypyrrole to PMMA-*co*-PNPAMs. However, those prepared from copolymers with a low content of NPAMs (<3 mol%) and of grafted polypyrrole (<20 mol%) showed some swelling in THF. Examination of the representative FTIR spectra (see Fig. 2) revealed that the absorption band at *ca.* 725 cm^{-1} attributed to C–H$_\alpha$ bending of the pyrrolyl

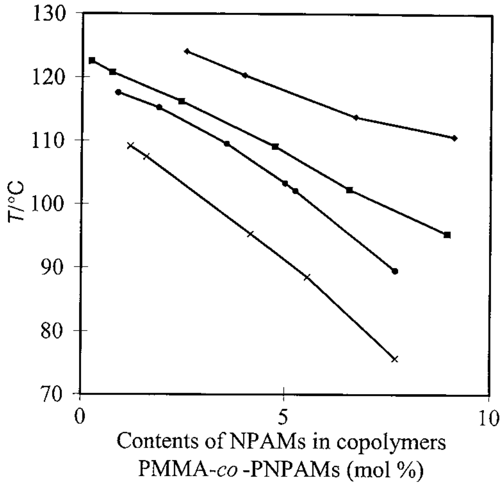


Fig. 1 Changes in T_g of the copolymers: (a) PMMA-*co*-PNPHM (◆); (b) PMMA-*co*-PNPOM (■); (c) PMMA-*co*-PNPDM (●); (d) PMMA-*co*-PNPDDM (×).

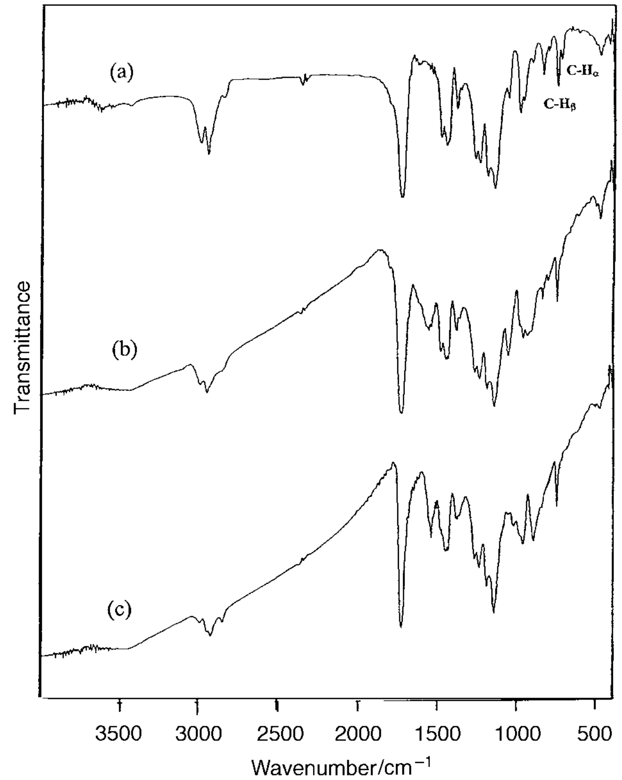


Fig. 2 FTIR spectra of: (a) PMMA-*co*-PNPDDM with a NPDDM content of 4.2 mol% prior to grafting with pyrroles; (b) its polypyrrole grafted copolymer containing 28.2 mol% of pyrrole; (c) poly(3-octylpyrrole) grafted copolymer containing 21.4 mol% of 3-octylpyrrole.

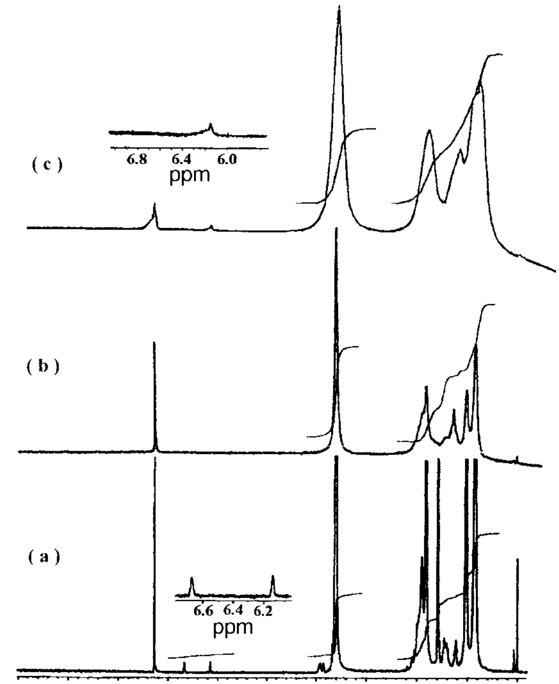


Fig. 3 ^{1}H NMR spectra of (a) copolymer of PMMA-*co*-PNPHM containing 2.6 mol% of PNPHM and the poly(3-dodecylpyrrole) grafted copolymer containing 19.0 mol% of 3-dodecylpyrrole at (b) a normal Relaxation Delay (RD) of 1 s; (c) when RD increased to 10 s.

Table 1 Shift in C=O stretching vibration of pyrroles grafted copolymers

Graft copolymers[a]	Contents of Py or 3APys/mol%	$\nu_{C=O}$/cm^{-1}
PMMA-*co*-PNPHM (6.7%)	20.4	1729
with pyrrole	28.9	1724
	33.6	1721
PMMA-*co*-PNPDDM (1.6%)	12.7	1733
with pyrrole	33.1	1720
PMMA-*co*-PNPHM (2.6%)	12.4	1731
with 3-octylpyrrole	23.4	1731
	31.1	1731
	39.9	1729

[a] The percentages in parentheses represent the content of NPAMs in PMMA-*co*-PNPAMs in mol%.

moieties in PMMA-*co*-PNPAMs had disappeared subsequent to the grafting reaction due to the coupling of pyrrole rings. The intense absorption band due to the ester carbonyl functionality at 1730 cm^{-1} was observed to have shifted to lower wavenumber with increasing polypyrrole content (Table 1). This phenomenon could be ascribable to the formation of NH···O=C hydrogen bonding between the grafted polypyrrole and the ester groups of the PMMA copolymers.[12c]

Table 2 summarises the electrical conductivity of the various polypyrrole grafted copolymers. The electrical conductivity

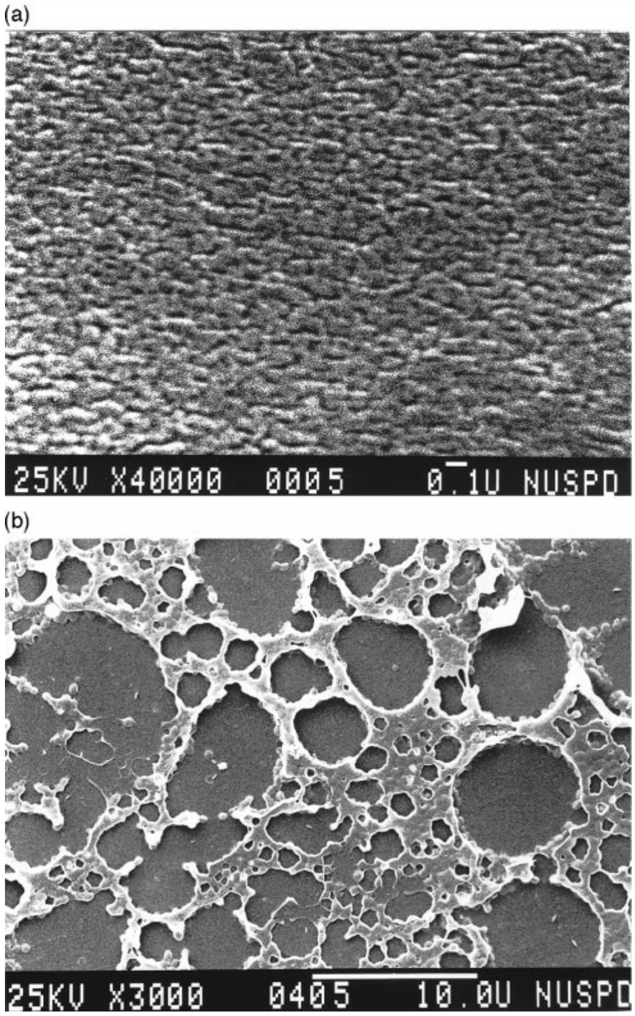


Fig. 4 Scanning electron microscopy (SEM) pictures of cast films of poly(3-alkylpyrrole) grafted onto PMMA-*co*-PNPHM containing 2.6 mol% of PNPHM: (a) poly(3-octylpyrrole) grafted copolymer containing 12.4 mol% of 3-octylpyrrole; (b) poly(3-decylpyrrole) grafted copolymer containing 24.7 mol% of 3-decylpyrrole.

Table 2 Properties of polypyrrole grafter copolymers of PMMA

Copolymers (PMMA-*co*-PNPAMs) used	Contents of NPAMs in PMMA-*co*-PNPAMs/ mol%	M_n of PMMA-*co*-PNPAMs/ g mol^{-1}	Feed ratio $C_{\mathrm{PNPAMs}}/C_{\mathrm{py}}$	Yield of graft copolymers (%)	Contents of Py in graft copolymers χ_{py}/ mol%	Conductivity[a]/S cm^{-1}	
						Pristine	Further doped with I_2
PMMA-*co*-PNPHM	2.6	41400	1/10	43	26.7	—	—
	2.6		1/40	46	47.1	3.0×10^{-4}	3.2×10^{-4}
	6.7	58600	1/5	57	20.4	—	—
	6.7		1/10	33	28.9	—	4.8×10^{-5}
	6.7		1/20	41	33.6	2.2×10^{-4}	3.1×10^{-4}
PMMA-*co*-PNPOM	0.2	44400	1/5	50	16.7	4.9×10^{-4}	5.4×10^{-4}
	0.2		1/10	33	24.5	5.6×10^{-4}	8.9×10^{-4}
	0.2		1/40	40	45.9	8.9×10^{-4}	7.8×10^{-4}
	2.4	43300	1/10	46	18.4	—	—
	2.4		1/40	59	36.1	3.9×10^{-4}	5.0×10^{-4}
PMMA-*co*-PNPDM	0.9	49300	1/10	58	23.4	—	—
	0.9		1/20	47	26.3	3.4×10^{-4}	3.2×10^{-4}
	0.9		1/40	43	44.2	6.0×10^{-4}	7.7×10^{-4}
	3.6	47400	1/10	56	21.1	—	—
	3.6		1/20	58	27.6	—	1.8×10^{-5}
	3.6		1/40	38	30.4	5.5×10^{-4}	8.3×10^{-4}
PMMA-*co*-PNPDDM	1.6	41400	1/20	60	33.1	—	—
	1.6		1/40	38	44.7	6.5×10^{-3}	7.8×10^{-3}
	4.2	52600	1/10	49	23.2	—	—
	4.2		1/40	52	29.7	1.2×10^{-4}	5.8×10^{-4}

[a] — means the conductivity is less than 1.0×10^{-5} S cm^{-1}.

was found to increase with increasing content of grafted polypyrrole attaining 10^{-4}–10^{-3} S cm^{-1} when the pyrrole contents were less than 50 mol%. Higher contents of grafted polypyrrole did not result in any significant increase in the conductivity. In addition, further doping with iodine at room temperature did not result in any distinct rise in conductivity, indicating that the graft copolymers had already been fully doped in the grafting process. There were no obvious effects arising from the use of different alkyl spacers in NPAMs or of varying the content of NPAMs in PMMA-*co*-PNPAMs on the electrical conductivity of the resultant graft copolymers.

The T_g values of some polypyrrole-grafted copolymers are depicted in Table 3. On comparing Fig. 1 with Table 3, it is clearly evident that T_g of the polypyrrole-grafted copolymers are somewhat higher than the corresponding PMMA-*co*-PNPAMs. In addition, T_g of the graft copolymers prepared from the same precursor copolymers PMMA-*co*-PNPAMs containing the same molar percentage of PNPAMs can be seen to increase with increasing grafted polypyrrole content. This indicates that pyrrole units grafted onto the PMMA chain have the effect of reducing the chain mobility of the resultant graft copolymers to some degree which consequently results in higher T_g.

Graft copolymers of PMMA with poly(3-alkylpyrrole)s

The graft copolymers from 3-alkylpyrroles having octyl, decyl, and dodecyl pendants with PMMA-*co*-PNPAMs also afforded black powders. Their key properties are summarised in Table 4. Their molecular weights (M_n) showed an apparently marginal increase in comparison to the precursor copolymers (PMMA-*co*-PNPAMs). It was found that the graft copolymers prepared from PMMA-*co*-PNPAMs having low NPAM contents (<2.6 mol%) were completely soluble in common organic solvents (THF, $CHCl_3$, and acetone) even in their doped states irrespective of the grafted poly(3-alkylpyrrole) (P3APy) content. Cast films of the P3APy grafted copolymers from their chloroform solutions on glass slides were examined using scanning electron microscopy (SEM) (see Fig. 4 for representative SEM pictures). At lower 3-alkylpyrrole contents, the graft

Table 3 T_g of polypyrrole grafter copolymers of PMMA

Copolymers (PMMA-*co*-PNPAMs) used	Contents of NPAMs in PMMA-*co*-PNPAMs/ mol%	M_n of PMMA-*co*-PNPAMs/ g mol^{-1}	Contents of grafted Py in copolymers χ_{py}/ mol%	T_g of graft copolymers/ °C
PMMA-*co*-PNPHM	2.6	41400	0	124.1
	2.6		26.7	130.0
	6.7	58600	0	113.8
	6.7		28.9	146.2
PMMA-*co*-PNPOM	2.4	43300	0	113.3
	2.4		8.1	119.2
	2.4		18.4	127.6
PMMA-*co*-PNPDM	0.9	49400	0	119.3
	0.9		23.4	122.2
	0.9		44.2	129.8
	3.6	47400	0	110.0
	3.6		13.1	113.5
	3.6		27.6	124.9
PMMA-*co*-PNPDDM	1.6	41400	0	118.3
	1.6		12.7	127.5
	1.6		33.1	132.8
	1.6		44.7	133.7
	4.2	52600	0	95.3
	4.2		16.4	122.8

Table 4 Properties of the poly(3-alkylpyrrole)s grafted copolymers of PMMA

3-Alkylpyrroles	Copolymers (PMMA-*co*-PNPAMs) used[a]	M_n of PMMA-*co*-PNPAMs/ g mol^{-1}	Feed ratio C_{PNPAMs}/C_{3APy}	Yield of graft copolymers (%)	Content of 3APy in graft copolymers/ mol%	M_n of graft copolymers/ g mol^{-1}	Conductivity[b] S cm^{-1}	Solubility[c]
3-Octylpyrrole	PMMA-*co*-PNPHM (2.6%)	41400	1/10	78	12.4	n.d.	—	+
			1/20	81	23.4	n.d.	4.8×10^{-4}	+
			1/30	89	31.1	42000	8.6×10^{-4}	+
	PMMA-*co*-PNPOM (0.2%)	44400	1/10	88	12.4	n.d.	—	+
			1/20	79	18.9	n.d.	8.8×10^{-5}	+
	PMMA-*co*-PNPDM (0.9%)	49300	1/10	75	11.8	n.d.	—	+
			1/20	80	25.5	50100	1.3×10^{-4}	+
	PMMA-*co*-PNPDDM (1.6%)	41400	1/10	88	13.6	n.d.	—	+
			1/20	90	20.2	n.d.	1.0×10^{-4}	+
	PMMA-*co*-PNPDDM (4.2)	52600	1/10	90	13.9	—	—	±
			1/20	88	21.4	—	2.3×10^{-4}	±
	PMMA-*co*-PNPDDM (7.7%)	49800	1/10	89	19.4	—	—	–
			1/20	86	24.0	—	1.2×10^{-4}	–
3-Decylpyrrole	PMMA-*co*-PNPHM (2.6%)	41400	1/20	78	24.7	42300	3.0×10^{-4}	+
	PMMA-*co*-PNPOM (0.2%)	44400	1/20	81	21.4	n.d.	1.3×10^{-4}	+
	PMMA-*co*-PNPDM (0.9%)	49300	1/20	79	18.3	n.d.	1.2×10^{-4}	+
	PMMA-*co*-PNPDDM (1.6%)	41400	1/20	86	20.2	42100	2.3×10^{-4}	+
3-Dodecylpyrrole	PMMA-*co*-PNPHM (2.6%)	41400	1/20	87	19.0	n.d.	2.5×10^{-4}	+
	PMMA-*co*-PNPOM (0.2%)	44400	1/20	84	19.4	44800	8.0×10^{-4}	+
	PMMA-*co*-PNPDM (0.9%)	49300	1/20	85	20.2	n.d.	2.5×10^{-4}	+
	PMMA-*co*-PNPDDM (1.6%)	41400	1/20	90	19.5	42100	3.9×10^{-4}	+

[a] The percentages in parentheses represent the content of NPAMs in PMMA-*co*-PNPAMs in mol%. [b] — means the conductivity is less than 1.0×10^{-5} S cm^{-1}. [c] Refers to solubility in $CHCl_3$, THF, and acetone: '+' completely soluble; '±' partially soluble; '–' insoluble. n.d. means not determined.

copolymers appeared homogeneous suggesting the grafted P3APy to have completely dissolved into the PMMA-*co*-PNPAM copolymers (Fig. 4a). However, at higher P3APy contents, the graft copolymers displayed a globular network structure (Fig. 4b) which could be attributed to phase separation/aggregation of the P3APy component in the graft copolymers. This observation is suggestive that at lower 3-alkylpyrrole contents, homogeneous grafted copolymers resulted whereas at higher contents, an apparently incompatible polymer blend between two polymers resulted.

As with polypyrrole grafted copolymers the FTIR spectra of P3APy (Fig. 2c) grafted materials revealed the disappearance of the C–H_α bending vibrational band indicative of a successful grafting process *via* α–α couplings of P3Apy to the pyrrolyl moieties in PMMA-co-PNPAMs. Further corroboration for this was provided from the disappearance of the α-proton signal in the ^{1}H NMR spectra of the representative poly(3-dodecylpyrrole) grafted copolymers (Fig. 3). However, the signal at *ca.* 6.15 ppm due to the β-protons of the pyrrolyl moiety also disappeared. This phenomenon was also previously observed by Stanke *et al.*[12b,16b] and was attributed to the formation of aggregates and slow relaxation of the said resonance.[17, 18] In our samples, we have verified the existence of the pyrrolyl β-protons by conducting NMR experiments with the relaxation delay increased to 10 seconds, whereupon the δ 6.15 β-proton signal reappears (Fig. 3c and the inset). Unlike the graft copolymers from unsubstituted pyrrole, the carbonyl band in FTIR spectra of the soluble graft copolymers did not show any significant shift to lower wavenumbers with increasing content of 3APy (Table 1). This could be ascribable to the formation of NH···O=C hydrogen bonding being disfavoured by the steric effects of the *n*-alkyl pendants attached. Similarly, steric effects of the pendant chains which prohibit crosslinking between pyrrole rings may also be the cause of the great improvement in the solubility of 3APy grafted copolymers. With increasing contents of NPAMs in PMMA-*co*-PNPAMs, the solubility of the resultant graft copolymers decreased. Thus, the graft copolymers of 3-octylpyrrole with PMMA-*co*-PNPDDMs were completely soluble, partially soluble and insoluble when the content of NPDDM in PMMA-*co*-PNPDDMs was increased from 1.6 to 4.2 and then 7.7 mol%, respectively (Table 4). This could be attributed to the crosslinking between NPAM units, which is more likely with increasing content of NPAMs in PMMA-*co*-PNPDDMs.

As with the polypyrrole grafted copolymers, the conductivity of the P3APy grafted copolymers increases with the content of P3APys attaining *ca.* 10^{-4} S cm^{-1} at about 20 mol%. Thereafter, further increase in the content of 3APys did not result in any further increase of the conductivity of the resultant graft copolymers as evident in Table 4 from the representative experimental results based on the graft copolymer of 3-octylpyrrole and PMMA-*co*-PNPHM (containing 2.6 mol% NPHM). Further, from Table 2 and 4, the introduction of long alkyl groups onto the 3-position has only marginal influence on the conductivity of the resultant graft copolymers.

Conclusions

Pyrrole and 3-alkylpyrroles were grafted to the precursor copolymers of PMMA and NPAMs by effecting an oxidative polymerisation with $FeCl_3$ in nitromethane. The electrical conductivity of the graft copolymers increases with increasing pyrrole or 3-alkylpyrroles content attaining *ca.* 10^{-4}–10^{-3} S cm^{-1}. The carbon chain lengths of the *n*-alkyl spacers between pyrrole and the methacrylate groups in NPAMs had little effect on the conductivity of the resultant graft copolymers, though longer alkyl spacers have an effect of lowering the glass transition temperatures of the polypyrrole grafted copolymers. The graft copolymers of polypyrrole were insoluble, whilst the graft copolymers of 3-alkylpyrroles prepared from low NPAM-containing PMMA-*co*-PNPHMs and low 3-alkylpyrroles contents were completely soluble in common organic solvents even in their doped states. The introduction of long alkyl pendants onto the 3-position of pyrrole was shown to have little influence on the conductivity of the resultant graft copolymers.

We thank the National University of Singapore for financial support through the research grant RP960613. W.-L. Yu is grateful to NSTB for a postdoctoral research fellowship and J. F. Xia to NUS for the award of a research studentship.

References

1 G. Tourillon, *Handbook Of Conducting Polymers*, ed. T. A. Skotheim, Marcel Dekker, NY, 1986.

2 A. G. MacDiarmid and A. J. Epstein, *Faraday Discussions*, 1989, **88**, 317.

3 E. M. Genies, A. Boyle, M. Lapkowski and C. Tsintavis, *Synth. Met.*, 1990, **36**,139.

4 M. G. Kanatzidis, *Chem. Eng. News*, 1990, Dec 3, 36.

5 A. O. Patil, A. J. Heeger and F. Wudl, *Chem. Rev.*, 1988, **29**, 183.

6 N. Toshima and S. Hara, *Prog. Polym. Sci.*, 1995, **20**, 155.

7 A. I. Nazzal and G. B. Street, *J. Chem. Soc.*, *Chem. Commun.*, 1985, 375.

8 J. H. Han, T. Motobe, Y. E. Whang and S. Miyata, *Synth. Met.*, 1991, **45**, 261.

9 G. Ruggeri, E. Spila, G. Puncioni and F. Ciardelli, *Macromol. Chem.*, *Rapid Commun.*, 1994, **15**, 537.

10 V. Castelvetro, A. Colligiani, F. Ciardelli, G. Ruggeri and M. Giordano, *New Polymeric Mater.*, 1990, **2**, 93.

11 M. R. Simmons, P. A. Chaloner and S. P. Armes, *Langmuir*, 1995, **11**, 4222.

12 (*a*) D. Stanke and M. L. Hallensleben, *Synth. Met.*, 1993, **55–57**, 1108; (*b*) D. Stanke, M. L. Hellensleben and L. Toppare, *Synth. Met.*, 1995, **72**, 89; (*c*) *ibid.*, 1995, **73**, 1; (*d*) *ibid.*, 1995, **72**, 61; (*e*) D. Stanke, M. L. Hellensleben and L. Toppare, *Macromol. Chem. Phys.*, 1995, **196**, 1697.

13 S.-K. Kang, W.-S. Kim and B.-H. Moon, *Synthesis*, 1985, 1161.

14 J. Ruhe, T. Ezquerra and G. Wegner, *Makromol. Chem.*, *Rapid Commun.*, 1989, **10**, 103.

15 E. P. Papadopoulos and N. F. Haidar, *Tetrahedron Lett.*, 1968, **14**, 1721.

16 (*a*) D. Stanke, M. L. Hallensleben and L. Toppare, *Synth. Met.*, 1995, **72**, 167; (*b*) D. Stanke, M. L. Hallensleben and L. Toppare, *Synth. Met.*, 1995, **73**, 267.

17 G. L. Baker and F. S. Bates, *Macromolecules*, 1984, **17**, 2619.

18 B. Bidan and M. Guglielmi, *Synth. Met.*, 1986, **15**, 49.

Paper 8/06438E