Poly(3-alkylthiophene)s as Anticorrosive Additive for Paints: Influence of the Main Chain Stereoregularity

José I. Iribarren,[1] Cintia Ocampo,[1] Elaine Armelin,[1] Francisco Liesa,[2] Carlos Alemán[1]

[1]*Departament d'Enginyeria Química, E.T.S. d'Enginyeria Industrial de Barcelona, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona E-08028, Spain*
[2]*Departament d'Enginyeria Mecànica, E.T.S. d'Enginyeria Industrial de Barcelona, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona E-08028, Spain*

ABSTRACT: The influence of the main chain stereoregularity on the properties of poly(3-decylthiophene-2,5-diyl) as anticorrosive additive of conventional organic coatings have been examined. For this purpose a small concentration (0.3% w/w) of regiorandom and regioregular conducting polymers were added to alkyd, epoxy, and polyurethane paints typically used in marine environments. The Young's modulus and the elongation at break of the alkyd and epoxy coatings modified with the regiorandom conducting polymer were significantly better than those of the films generated with the original paints, evidencing a very favorable interaction between the additive and the resins. On the other hand, the anticorrosive properties imparted by the modified paints are better when the conducting polymer is regiorandom than when it is regioregular, although even the degree of protection provided by all the modified coatings was higher than that of the original ones. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3291–3297, 2008

Key words: additives; coatings; conducting polymers

INTRODUCTION

In the past few years poly(3-alkylthiophene)s (P3ATs) have attracted much attention because of their solubility, fusibility, processability, electrical and electroluminescent properties, and nonlinear optical activity.[1–4] However, the properties of P3ATs strongly depend on the relative orientation of monomeric units when thiophene rings are coupled between the 2 and 5 positions. Specifically, three different couplings are possible: head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT). In the latter two linkages, a sterically driven twist of the thiophene rings causes the breakdown of the planarity of the main chain, which results in a loss of conjugation. In contrast, HT couplings can easily access to a low-energy planar conformation with a high degree of conjugation. Consequently, the electrical and optical properties of regioregular HT-coupled polymers are significantly better than those of regiorandom polymers. Furthermore, HT regioregularity enhances significantly the crystallinity of main chains in P3ATs.[3,5,6] Thus, polythiophene chains tend to adopt a planar conformation in ordered semicrystalline arrangements.

On the other hand, P3ATs bearing long alkyl side chains, i.e., $n \geq 6$ where n indicates the number of carbon atoms of the alkyl side chain, show a crystalline fraction associated to the side-by-side packing of these flexible paraffinic groups, which act as spacers between the stiffer polythiophene main chains.[7–10] This structure is similar to that described for conventional comb-like polymers.[11–13] Moreover, a polymorphic behavior for these P3ATs has been reported.[14–17]

A very promising technological application of P3ATs consists on their use as anticorrosive additive for paint formulations.[18] Thus, we recently found that modification of paints by the addition of a low concentration (0.2–0.4% w/w) of conducting polymer, which can be polyanilinine,[19,20] polypyrrole,[21] or polythiophene derivatives,[22,23] increases significantly the protective properties of the coating. The use of conducting polymers as anticorrosive additive present some advantages with respect to conventional inorganic anticorrosive pigments: reduction of solid contents, reduction of contaminants, better adherence of the coating, etc. The miscibility of the conducting polymer in the paint is a determinant factor for this new application of electroactive materials. Thus, to obtain homogeneous emulsions of the modified paint, the incorporation of substituents able to facilitate the solubility of the conducting

polymer in the paint dispersion was proved to be a very valuable strategy.[18]

One of the most successful conducting polymer for anticorrosion applications was found to be regioregular poly(3-decylthiophene-2,5-diyl), hereafter denoted reg-P3DT.[22] Thus, the long flexible decyl side groups of reg-P3DT improves the miscibility of the polycyclic chains in paint dispersions, especially those based on organic solvents. Accelerated laboratory corrosion tests indicated that the addition of reg-P3DT to different epoxy formulations significantly improves the degree of protection imparted by the films of coating. Thus, we observed that the amount of oxide particles detected at the surface of the steel pieces coated with the modified primers was noticeably lower than that found in the films without conducting polymer.

In this work, we investigate the influence of the backbone stereoregularity of P3DT on the ability of this material to act as an anticorrosive additive of conventional organic coatings. Results are important to understand phenomenological detains about the interactions between the resins contained in the formulation of the primers and both the side chain and main chain of the conducting polymer. The organic coatings used for the assays consist of different primers typically used in marine environments, which have been modified by the addition of a low concentration of conducting polymer. Specifically, the degree of protection imparted by reg-P3DT and regiorandom P3DT, hereafter denoted ran-P3DT, has been examined and compared. As the physical properties and characteristics of both the conducting polymers[1,7–17] and the paint coatings[24] used in this work have been reported in previous studies, we mainly concentrate on the analysis of the results provided by accelerated laboratory immersion tests of steel pieces coated with the original and modified paints.

METHODS

The conducting polymers, reg-P3DT and ran-P3DT, were purchased from Sigma-Aldrich (Madrid, Spain) (average $M_w \sim 42,000$, average $M_n \sim 30,000$). The coatings for marine and protective use that have been used in this work are an alkyd primer, a two-component cured epoxy resin, and a two-component polyurethane primer. The rheological properties of these coating were previously characterized and described.[24] The elemental weight composition of the carbon steel (St F111) used as metallic substratum in corrosion experiments is as follows: C < 0.08%, Mn = 0.25%, Si = 0.01%, P = 0.014%, and Al = 0.014%. Other remarkable characteristics determined in our laboratory for this steel are as follows:

(a) density = 7.86×10^3 kg/m^3; (b) medium rugosity = 1.9 μm; (c) maximum rugosity = 12.6 μm. Rectangular test pieces of 40 mm × 48 mm × 2 mm with a diameter hole of 4 mm were degreased with acetone and stored in dry atmosphere before use.

The paints were applied by immersion of the metallic pieces in a primer/solvent/hardness composition with the manufacturer's recommended mixing ratio. This procedure yielded samples with a film thickness of around 160–200 μm after one coat, which was determined using a thickness measurement machine model Uno-Check Fe.

A Bomem Michelson MB100 FTIR spectrophotometer, with a resolution of 4 cm^{-1} in the absorbance mode, was employed for the characterization of the coatings films. The samples were placed in an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma). Thermogravimetric analyses were carried out with a Perkin-Elmer TGA-6 thermobalance at a heating rate of 10°C/min, from 30 to 850°C temperature range and under nitrogen atmosphere.

Mechanical properties were evaluated with a Zwick Z2.5/TN1S testing machine. Regular films were prepared by evaporation of the volatile organic solvent of the paint formulation at room temperature. Plate samples with a length of 30 mm and a width of 3 mm were cut out from the films and used in stress–strain experiments. The thickness of the samples used in this case was 300–350 μm. The deformation rate was 10 mm/min. Mechanical parameters like Young's modulus, tensile strength, and elongation at break were averaged out at 10 measurements for each paint film.

Corrosion studies were carried out with a homemade equipment developed at our laboratory for accelerated corrosion tests.[25] It consists of a support to put steel pieces, which is controlled by a programmable device, and a bath containing an aggressive solution medium. This device allows program-controlled cycles formed by the following steps: immersion, wringing, drying, and cooling. The corrosive solution medium consists of an aqueous solution of NaCl (3.5 wt %, pH 6.6). The operating conditions for one cycle are as follows: immersion of the painted steel pieces into the solution (15 min), wringing of the steel pieces (30 min), drying forced with bulbs (230 V to 100 W, 10 min), and cooling at room temperature (5 min). Painted panels were sealed on the edges and around the hole used for securing the pieces. The samples were tested in the solution medium during 720 h. The complete set up was maintained at 25°C. The evolution of the paint degradation was followed by FTIR analysis and surface reflection optical microscopy. Micrographs were taken using an Olympus BX-5 light polarizing

TABLE I
Characteristics of the Two P3DT Used in the Work

	Composition	Structure and color of cast films	κ (S/cm)[a]	ε_g (eV)[b]
reg-P3DT	98.5% HT	Crystalline, flexible, and bronze-colored	1×10^{-6}	1.7
ran-P3DT	1 : 1 HH : HT	Amorphous and orange-colored	1×10^{-9}	2.1

[a] Electrical conductivity.
[b] π–π* transition energy (gap).

microscope, operating in reflection mode coupled with an Olympus C3030Z digital camera.

RESULTS AND DISCUSSION

Table I summarizes the main characteristics of both reg-P3DT and ran-P3DT.[1,7–17] As can be seen, the electronic and electroelectrical properties of the former material are significantly better than those of the latter one. On the other hand, the thixotropic behavior of the original coatings[24] was recently reported.

Modified coatings were prepared by adding a low concentration of conducing polymer (0.3% w/w) to the paint formulation. Homogeneous emulsions were achieved by previous dispersion of P3DT in carbon tetrachloride (0.1 g of polymer/5 mL of solvent) and mechanical stirring of the mixtures. It should be mentioned that the dispersion of the conducting polymer on the paint is significantly better with this solvent than with chloroform. Thus, in our previous study the reg-P3DT polymer, which dissolved in a minimal volume of chloroform, precipitated when added to the epoxy paint forming solid aggregations at the surface of the liquid paint.[22] However, in this study homogeneous mixtures of the epoxy coating with both reg-P3DT and ran-P3DT were achieved.

To check that the addition of a small concentration of reg-P3DT and ran-P3DT does not alter the physical characteristics of the paints, properties of the modified coatings have been determined and compared with those obtained for the original ones. Figure 1 compares the FTIR spectra of the original and the modified paints, no significant difference being detected among them. The interpretation of the polymeric resins used in paint formulation is usually difficult because of the appearance of bands from pigments and/or additives. In spite of this, the more representative absorption bands (Table II) of the alkyd, epoxy, and polyurethane resins studied in this work are shown in Figure 1.

On the other hand, the thermogravimetric curves of the original paints remained unaltered after the addition of P3DT (data no shown). Thermogravimetric analyses of the coatings from 30 to 850°C indicated that the amount of inorganic pigments and/or

additives is very similar for the three formulations, ranging from 50 to 55%.

Figure 2 compares the stress–strain curves of the original and modified alkyd, epoxy, and polyurethane coatings, the resulting stress–strain parameters being
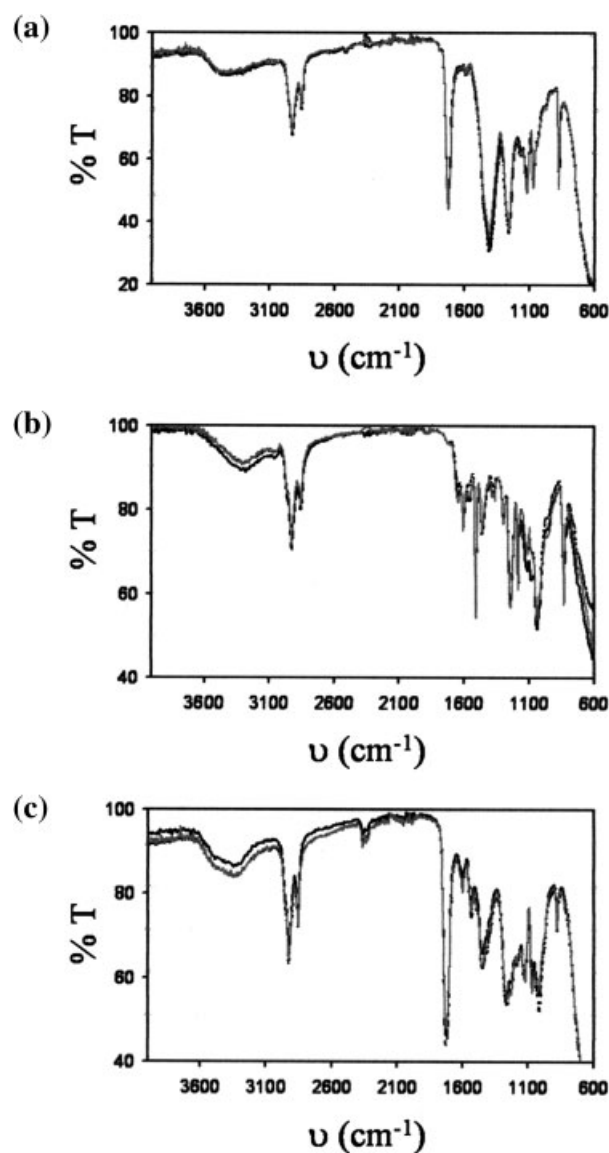

Figure 1 FTIR spectra of original and modified alkyl (a), epoxy (b), and polyurethane (c) paints: original (continuous black line), modified by the addition reg-P3DT (dashed black line), and modified by the addition ran-P3DT (continuous gray line).

TABLE II
Absorption Bands in the Infrared Spectra for the Paint Films Studied in this Work

Description	Absorption band (cm^{-1})	
Alkyd resin	3441	O—H
	2924, 2854	C—H
	1724	C=O (ester)
	1434	CH$_2$
	1257, 1119	C—O (ester)
	1072	P—O (PO$_4{}^{2-}$)
Epoxy resin	3279	N—H
	2924, 2958	C—H
	1608, 1508	C=C
	1458, 1385	CH$_2$, CH$_3$
	1242, 1028	C—O—C (ether)
	1182	R—CH—O—CH—R (ether)
	827	C—H (Ar p-substituted)
Polyurethane	2924, 2854	C—H
	1724	C=O (urethane)
	1535, 1454	CH$_2$, CH$_3$
	1245–1037	C—N and C—O (urethane)

listed in Table III. As can be seen, all the original and modified paints are brittle materials with high Young's modulus and low elongation at break. However, the addition of a small concentration of P3DT produces some alterations in the mechanical properties of the coating films. Furthermore, the influence of the conducting polymer depends on its regioregularity. Specifically, the addition of ran-P3DT to the alkyd and epoxy paints produces an improvement of both the Young's modulus and the elongation at break, while mechanical properties remain more or less unaltered upon addition of reg-P3DT. The overall results should be attributed to the main chain crystallinity of reg-P3DT, which reduces the miscibility of the conducting polymer with the paint. Accordingly, ran-P3DT interacts better with the alkyd and epoxy resins than reg-P3DT altering the mechanical properties of the original paint films. On the other hand, the modulus of elasticity in tension of the original polyurethane coating is higher than those of the two modified films, which also show a remarkable reduction of the tensile strength. However, also in this case the mechanical properties of the films modified with reg-P3DT are, in general, slightly worse (especially the elongation at break) than those of the coating modified with ran-P3DT. It should be noted that the interaction of the polyurethane resin with P3DT is, independently of the stereoregularity of the main chain, worse than with the epoxy and alkyd paints, which led to increase the brittleness of the modified films with respect to the original ones. Furthermore, we observed that the mechanical properties of modified polyurethane get even worse when the concentration of conducting polymer is increased.

All the steel panels coated with original and modified paints were ascribed according to the ASTM Standard Method D-1654 before the accelerated exposure tests. This method allows solution droplets to run lengthwise along the scribe. The ascribed panels were exposed to an aggressive solution during 720 h as is described in the Methods section, evaluations being performed after 120, 240, 480, and 720 h. At every evaluation interval 18 panels, two per each type of coating, were extracted for subsequent analysis. Figures 3 and 4 show the photographs and
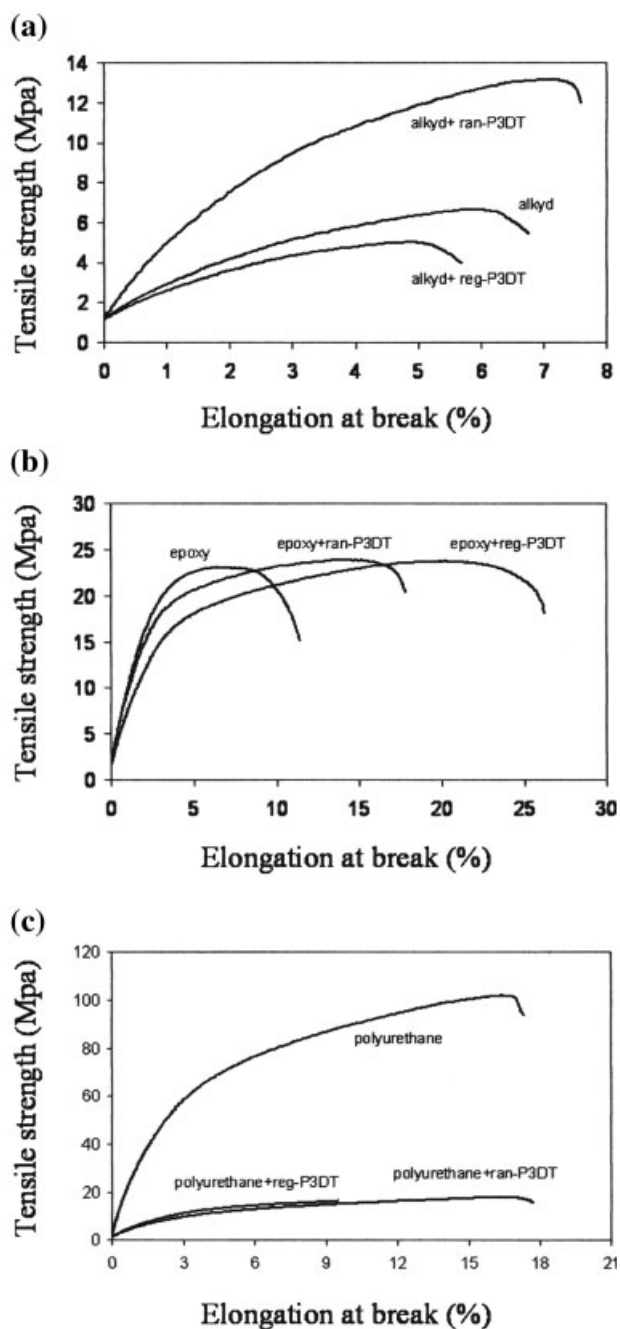

Figure 2 Tensile stress–strain curves of the original and modified (a) alkyd, (b) epoxy, and (c) polyurethane paints.

TABLE III
Mechanical Properties for the Original and Modified Paints Studied in this Work: Young's Modulus (E), Tensile Strength (σ_{max}), and Elongation at Break (ε_b). Properties for High-Density Polyethylene (HDPE) and Polypropylene (PP) Have Been Included for Comparison

Material		E (MPa)	σ_{max} (MPa)	ε_b (%)
Alkyd	Original	148	7	7
	+reg-P3DT	121	5	6
	+ran-P3DT	399	13	12
Epoxy	Original	867	23	11
	+reg-P3DT	673	24	26
	+ran-P3DT	1016	24	18
Polyurethane	Original	1991	102	17
	+reg-P3DT	406	14	9
	+ran-P3DT	449	18	18
HDPE		1070–1090	22–31	10–1200
PP		1170–1720	31–41	100–600

Figure 4 Optical micrographs from the polymeric films after 720 h of accelerated corrosion assays (scale bar: 200 μm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

micrographs, respectively, of the panels after 720 h of accelerated corrosion tests. Comparison of the three original paints reveals that, as expected, the epoxy and polyurethane paints impart greater protection against corrosion than the alkyd one. Thus, after 30 days of accelerated corrosion assays the pieces coated with the two former formulations, which are typically used to protect metallic substrates of marine environments, evidence a notable resistance against corrosion.

On the other hand, comparison of the photographs and micrographs of the panels coated with the original and modified paints reveals that for the polyurethane and, especially, the alkyd paint, the anticorrosive properties imparted by ran-P3DT are higher than those provided by reg-P3DT. Furthermore, the protecting role of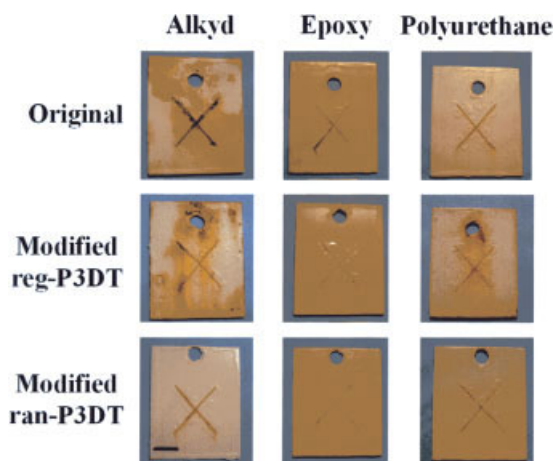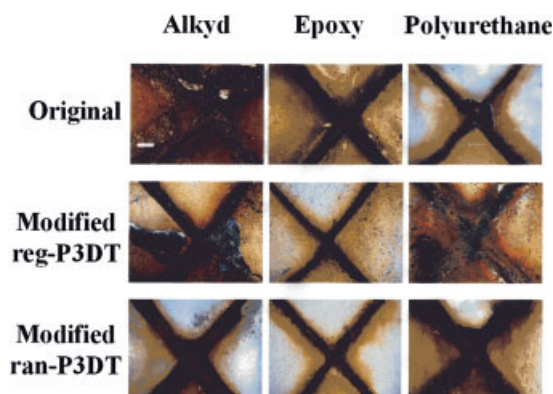 ran-P3DT is very active along the whole accelerated corrosion assay. This is evidenced for the alkyd paint modified with ran-P3DT in Figure 5, which compares the photographs and micrographs of the panels extracted at each evaluation interval. It is worth noting that the corrosion process is significant in the panels coated with the original paint after 240 h. However, after 480 h the corrosion process is very small for the panels coated with the alkyd paint modified with a small concentration of ran-P3DT. Regarding to the epoxy paint, the protecting role imparted by the conducting polymers is less apparent than for the alkyd and polyurethane coatings. This is because organic coatings based on epoxy resins provides a significant protection by their own, being considered as the best paints to protect steel and iron from corrosion in marine environments.[18]
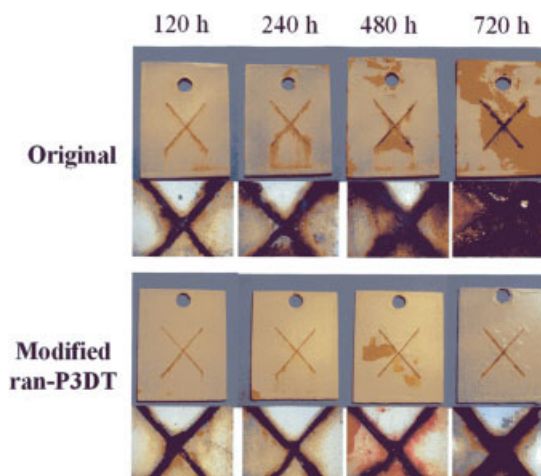

Figure 3 Photographs of the painted rectangular panels after 720 h of accelerated corrosion assays (scale bar: 1 cm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Optical photographs (scale bar: 1 cm) and micrographs (scale bar: 200 μm) from both original and modified with ran-P3DT polyurethane films at different evaluation intervals of the accelerated corrosion assays. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
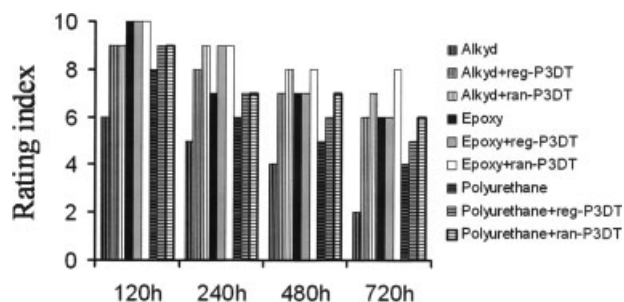
Figure 6 Evolution of the rating index describing the loss of adherence (ASTM D-1654-79a procedure) against the exposure time to accelerated corrosion assays for the original and modified paints.

The loss of adherence associated with corrosion was evaluated according to the procedure indicated in the ASTM D 1654-79 method. For this purpose, the panels were scraped vigorously with a rigid metal spatula, which was faced perpendicular to the specimen surface and parallel to the scribe. Moving of the spatula back and forth across the scribe allowed to remove the coating that suffered loss of adhesion only without removing the coating that still has adhesion. Then, the loss of adherence was converted in a rating index that ranges from 0 to 10, the former and latter value indicating complete and no loss of adherence, respectively. Figure 6 shows the evolution of this rating index for the original and modified coatings against the time of exposure to the saline solution. As can be seen, results are fully consistent with the photographs and micrographs displayed in Figures 3 and 4, respectively. Thus, the corrosion protection is enhanced by the addition of conducting polymer, which leads to reduce the corroded area in the modified paints modified with respect to the original ones. Furthermore, this improvement is quantitatively higher for the paints containing ran-P3DT than for those modified with reg-P3DT. On the other hand, the most remarkable enhancement of the corrosion protection is observed for the alkyd coating, this feature being evidenced only after 120 h of exposure to the saline solution.

In summary, the complete miscibility of reg-P3DT in the studied paints seems to be precluded by the main chain crystallinity. As a consequence, although the degree of protection against corrosion imparted by coatings modified with reg-P3DT is higher than that of the original paints, it can be improved by intensifying the favorable interactions between the conducting polymer and the resins. This occurs when the stereoregularity of the main chain is lost. Thus, the addition of ran-P3DT, which is not able to adopt an ordered main chain structure, to the coatings produces an improvement of both the mechanical properties and the anticorrosive properties not only with respect to original paints but also with

respect the paints modified with reg-P3DT. It should be remarked that the structure of the decyl side groups is very similar for both reg-P3DT and ran-P3DT[7–10,14–17] indicating that, when these two polymers are used as additives of conventional organic coatings, the differences in their behavior must be attributed exclusively to the main chain stereoregularity. Thus, the amorphous nature of ran-P3DT induces favorable interactions with the resin allowing their complete miscibility, this feature being responsible for the excellent results obtained when this polymer is used as additive. In contrast, the crystallinity of reg-P3DT precludes a complete miscibility with the resin, which produces a reduction of the corrosion protection with respect to ran-P3DT.

CONCLUSIONS

Homogeneous emulsions were prepared by adding a low concentration (0.3% w/w) of reg-P3DT and ran-P3DT to alkyl, epoxy, and polyurethane paint formulations. The structural and thermal characteristics of the modified coatings were almost identical to those of the original paints as revealed by FTIR and thermogravimetric analyses. However, the mechanical properties of the paints underwent some alterations after the addition of the ran-P3DT conducting polymer. Specifically, the Young's modulus and the elongation at break of the alkyd and epoxy paints modified with ran-P3DT were higher than those of the original films. These facts were attributed to the good miscibility of ran-P3DT with these resins, while the main chain crystallinity of reg-P3DT precludes such miscibility. In contrast, the mechanical properties of the original polyurethane films were better than those of the two modified coatings indicating that, independently of the main chain stereoregularity, the miscibility of the conducting polymer with this paint was poor.

On the other hand, analysis of the panels coated with the original and modified paints after accelerated corrosion analyses revealed that, independently of its stereoregularity, the addition of a small concentration of P3DT to the paint formulations provides an improvement of their anticorrosive properties. The positive influence of the conducting polymer was especially evident in alkyd and polyurethane paints, and the anticorrosive performance of the epoxy paints is intrinsically high. Furthermore, the degree of protection against corrosion imparted by the paints modified with ran-P3DT is significantly better than those of the paints modified with reg-P3DT. This should be attributed to the favorable interaction between the resins and both the side chain and main chain of ran-P3DT, which is not possible when the main chain is regioregular.

References

1. Chen, T. A.; Wu, X.; Rieke, R. D. J Am Chem Soc 1995, 117, 233.
2. Hsu, W.-P.; Levon, K.; Ho, K.-S.; Myerson, A. S.; Kwei, T. K. Macromolecules 1993, 26, 1318.
3. Yang, C.; Orfino, F. P.; Holdcroft, S. Macromolecules 1996, 29, 6510.
4. McCullough, R. D. Adv Mater 1998, 10, 93.
5. Malik, S.; Nandi, A. K. J Polym Sci Part B: Polym Phys 2002, 40, 2073.
6. Daoud, W. A.; Xin, J. H. J Appl Polym Sci 2004, 93, 2131.
7. Prosa, T. J.; Winokur, M. J.; Moulton, J.; Smith, P.; Heeger, A. J. Macromolecules 1992, 25, 4364.
8. Tashiro, K.; Kobayashi, M.; Kawai, T.; Yoshino, K. Polymer 1997, 38, 2867.
9. Xie, H.; Corish, J.; Morton Blake, D. A. Synth Met 2000, 113, 65.
10. Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.-L.; Suganuma, H.; Asakawa, N.; Inoue, Y., Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. J Am Chem Soc 1998, 120, 2053.
11. Curcó, D.; Alemán, C. J Polym Sci Part B: Polym Phys 2006, 44, 953.
12. Curcó, D.; Alemán, C.; Rude, E.; Muñoz-Guerra, S. Biomacromolecules 2003, 4, 87.
13. Curcó, D.; Alemán, C. J Chem Phys 2004, 121, 9744.
14. Ho, K.-S.; Bartus, J.; Levon, K.; Mao, J., Zheng, W.-Y. Synth Met 1993, 55–57, 384.
15. Prosa, T. J.; Winokur, M. J.; McCullough, R. D. Macromolecules 1996, 29, 3654.
16. Meille, S. V.; Romita, V.; Caronna, T.; Lovinger, A. J.; Catellani, M.; Belobrzeckaja, L. Macromolecules 1997, 30, 7898.
17. Bolognesi, A.; Porzio, W.; Provasoli, A.; Botta, C.; Comotti, A.; Sozzani, P.; Simonutti, R. Macromol Chem Phys 2001, 202, 2586.
18. Armelin, E.; Oliver, R.; Liesa, F.; Iribarren, J. I.; Estrany, F.; Alemán, C. Prog Org Coat 2007, 59, 46.
19. Iribarren, J. I.; Cadena, F.; Liesa, F. Prog Org Coat 2005, 52, 151.
20. Armelin, E.; Ocampo, C.; Liesa, F.; Iribarren, J. I.; Ramis, X.; Alemán, C. Prog Org Coat 2007, 58, 316.
21. Iribarren, J. I.; Alemán, C.; Liesa, F.; Casanovas, J.; Alemán, C. Mater Corros 2006, 57, 683.
22. Ocampo, C.; Armelin, E.; Liesa, F.; Alemán, C.; Ramis, X.; Iribarren, J. I. Prog Org Coat 2005, 53, 217.
23. Liesa, F.; Ocampo, C.; Alemán, C.; Armelin, E.; Oliver, R.; Estrany, F. J Appl Polym Sci 2006, 102, 1592.
24. Armelin, E.; Martí, E.; Rude, E.; Labanda, J.; Llorens, J.; Alemán, C. Prog Org Coat 2006, 57, 229.
25. Iribarren, J. I.; Liesa, F.; Cadena, F.; Bilurbina, L. Mater Corros 2004, 55, 689.