DOI: 10.1002/ange.201004920

Dyes/Pigments

The Combined Synthesis and Coloration of Poly(lactic acid)**

*Robert O. MacRae, Christopher M. Pask, Lucy K. Burdsall, Richard S. Blackburn, Christopher M. Rayner, and Patrick C. McGowan**

With the continuing depletion of petrochemical feedstocks, it has become necessary to produce new, useful, and environmentally friendly polymers for a sustainable future.[1] Synthesis of a polyester from lactic acid was pioneered by Carothers in 1932 and developed by DuPont.[2] Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester derived from 100 % renewable sources,[3–5] and the polymer is compostable.[4] The production of PLA uses 20–50 % less fossil fuel resources than comparable petroleum-based fibers.[6] PLA is a particularly "green" polymer in terms of sustainability and degradation, two vital components of the 'cradle-to-grave' life cycle. Plants process atmospheric CO_2 and water through photosynthesis to make the raw materials from which the building blocks of PLA can be obtained; and composting converts PLA into CO_2, water, biomass, humus, and other natural substances (Figure 1). PLA is formed either by direct condensation of lactic acid, or, most effectively, via the cyclic intermediate dimer (lactide) through a catalyzed ring-opening polymerization (ROP) process.[3] Metal alkoxides are the most common catalysts employed in ROP of cyclic esters. Aluminum alkoxides have been shown to give a controlled and living polymerization of lactides through a so-called coordination/insertion mechanism.[7]

For a typical textile dyeing process, poly(ethylene terephthalate)[8] and PLA[9] (Figure 1) are initially scoured with detergent and alkali to remove hydrophobic auxiliaries (aids knitting and weaving), and then dyed with disperse dyes in an aqueous dyebath buffered to pH 4.5 using sodium acetate or acetic acid at 130 °C or 115 °C, respectively. To achieve acceptable wash fastness properties (ability of dye to adhere to material), "after-clearing" with reducing agents is employed to remove the excess dye. Reduction after-clearing has a significant detrimental environmental impact because of the strong alkaline conditions, large amounts of water used, and the discharge of high levels of sulfur with the wastewater.[10,11] There is also concern that effluent from disperse dyeing operations of the reduction after-clearing process contains by-products, particularly aromatic amines from the reduction of azo dyes, that have mutagenic and carcinogenic activity.[12,13]

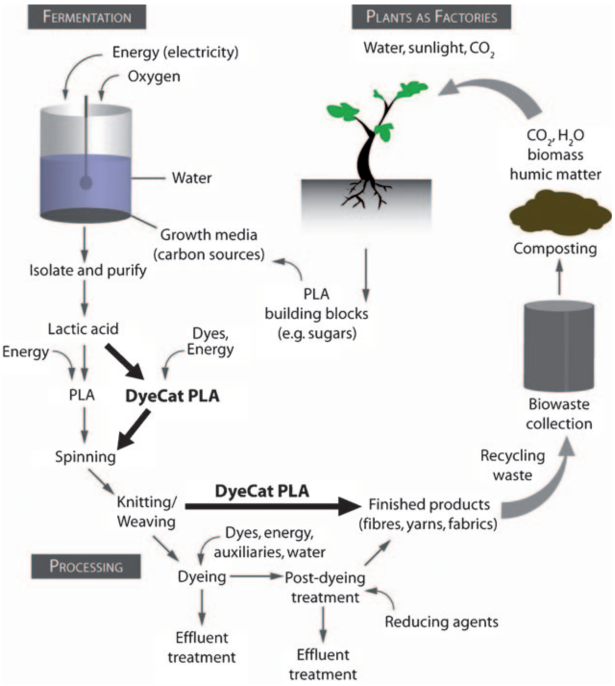


Figure 1. Life cycle of PLA for textile applications (Figure adapted from Gross and Kalra).[4]

Herein we report the use of a catalyst containing a chromophore, which will simultaneously carry out the polymerization, and in addition, incorporate the dye, needed to color the material, into the polymer backbone itself—termed the DyeCat process. Thus, the coloration process can achieve high color strength without exposing the fiber to potentially damaging conditions; these are two essential prerequisites for future commercial applications of PLA.

As shown in Figure 1, the wet processing stages (preparation, dyeing, finishing) are not required for DyeCat PLA because coloration is achieved through the polymerization process. Hence the consumption of energy, water, chemicals, and time, as well as effluent production are all avoided. Residual catalyst in the polymers can lead to undesirable polymer properties, including discoloration, and removal of the spent catalyst from a polymer is often difficult and

---

[*] R. O. MacRae, L. K. Burdsall, C. M. Rayner, P. C. McGowan
School of Chemistry, University of Leeds
Leeds, LS2 9JT (UK)
E-mail: P.C.McGowan@leeds.ac.uk
R. S. Blackburn
Centre for Technical Textiles, University of Leeds
Leeds, LS2 9 JT (UK)
C. M. Pask, R. S. Blackburn, C. M. Rayner, P. C. McGowan
DyeCat Ltd, 103 Clarendon Road, Leeds, LS2 9DF (UK)

[**] We wish to thank Yorkshire Forward, Techtran Ltd. and the University of Leeds for financial support. We would like to acknowledge B. Thomas and E. Gaston (University of Leeds) for help with Figure 1 and the table of contents graphic, respectively. We thank A. Hebden, C. Kilner, and J. Mannion for help with the crystallography.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004920.

expensive.[14,15] The paradigm shift for the process described herein is that the catalyst can be functionalized and deliberately left in the polymer.

Aluminum catalysts have a significantly lower environmental impact than their heavy-metal counterparts, and have been shown to be particularly effective at lactide polymerization.[16] We have identified three main strategies (and combinations thereof) for the incorporation of a dye into an aluminum catalyst structure: 1) a dye molecule may be appended to a ligand framework known to stabilize the Al center (Figure 2a), 2) a novel catalyst utilizing a known dye molecule as the ligand may be designed (Figure 2b), or 3) the dye may be used as the polymerization initiator (Figure 2c). These three complementary approaches have been investigated and all have been successful in producing colored PLA. As an exemplar of the DyeCat process, the method shown in Figure 2c will be discussed in detail. To synthesize the precatalyst, two equivalents of either $C_5H_4N(CO)NHC_6H_3F_2$ or $C_5H_4N(CO)NHC_6H_4NO_2$ were added to a solution of trimethylaluminium in toluene to yield pre-catalysts **1** and **2** (Figure 3). These were characterized using NMR spectroscopy, mass spectrometry, and elemental analysis, and X-ray crystallographic analysis for compound **2** (Figure S1 and Table S1 in the Supporting Information) shows a five-coordinate aluminum center having a square-pyramidal geometry. The compound **2** crystallized in a triclinic cell and the structural solution was performed in the space group $P\bar{1}$ (selected bond lengths and angles are given in Supporting Information).

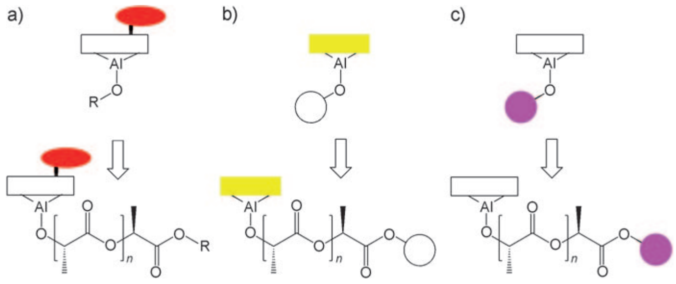
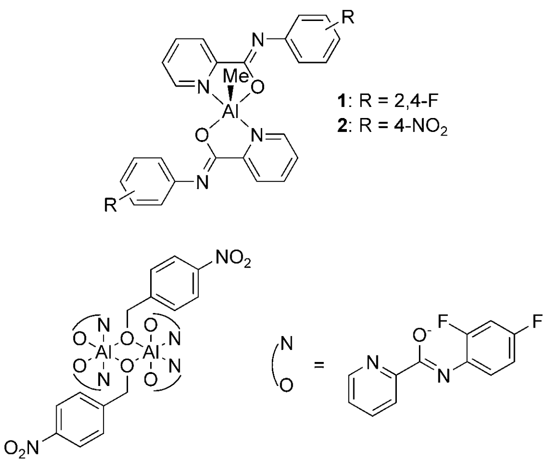


Figure 2. Three successful approaches for the DyeCat process. a) dye attached to ligand, b) dye as ligand, c) dye as initiator.



3

Figure 3. Precatalyst (**1** and **2**) used in polymerization reactions and proposed structure of a typical catalyst (**3**).

Aluminium alkoxide species have been implicated as the active species in PLA polymerization[16,17] and bimetallic zinc complexes containing a bridging aloxide have been proven to show high catalytic activity in lactide ring-opening polymerization.[18,19] Reaction of a *p*-nitrobenzylalcohol initiator with compound **1** forms the dimeric aluminium alkoxide species **3** (Figure 3) in the solid state, the crystal structure of which is shown in Figure 4. The molecular structure of compound **3** is dimeric, containing two aluminum centers bridged by two alkoxide ligands. Compound **3** crystallized in a monoclinic cell and the structural solution was performed in the space group $P2_1/n$ (selected bond lengths and angles are given in Supporting Information). A simple chemical modification of existing dye structures to incorporate functionality (e.g., primary alcohol group) required for initiation have been devised (e.g., **4**; Figure 5 and see the Supporting Information), and indeed some suitable dyes are already commercially available (e.g., **5**–**9**). Control reactions indicate that a polymer with a melting point of 172 °C (164 °C for in situ catalyst generation) and degree of crystallinity (x_c) of 45.5 % (44.6 % for in situ catalyst generation) is obtained using

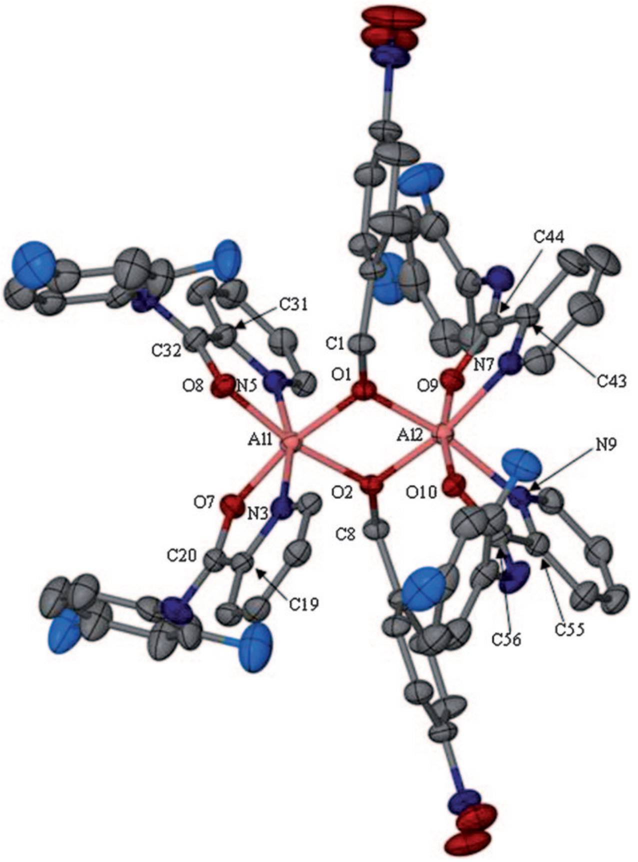


Figure 4. The molecular structure of compound **3**. Thermal ellipsoids are shown at the 50 % probability.

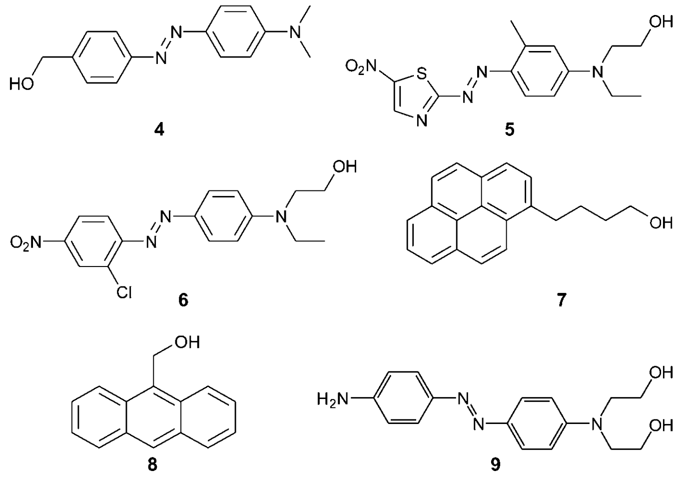


Figure 5. Initiators (**4**–**9**) used in the polymerization reactions.

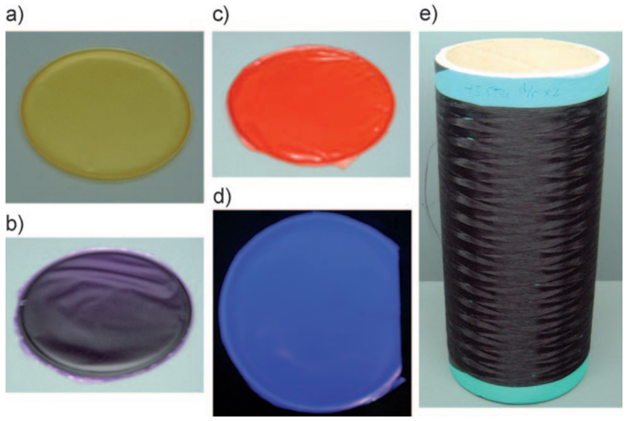


Figure 6. Examples of DyeCat PLA. The intiators used were **4** (a), **5** (b), **6** (c), **7** (d). e) Black melt-spun DyeCat filament.

compound **3** as the active catalyst; this is in comparison to the pre-catalyst **2** being treated with initiator and lactide.

To determine inclusion of the initiator within the polymer chain, polymerizations were conducted with a high catalyst loading to generate short-chain oligomers. These were probed by mass spectrometry, the results of which display a Boltzmann-like distribution of molecular weights. In the case of the benzyl alcohol initiator (see the Supporting Information) the molecular ion possesses the formula: $[NaH(OCOCH(CH_3))_nOCH_2Ph]^+$, with n ranging between five and twenty. The colored initiator **9** yields an ion with the formula: $[H_2(OCOCH(CH_3))_nOCH_2CH_2N(CH_2CH_2OH)C_6H_4N_2C_6H_4NH_2]^+$, with n ranging from one to fourteen. Therefore both mass spectra show incorporation of the initiator at the end of the oligomer chain. Overall, the characterization data provide compelling experimental evidence for the formation of the pre-catalyst, catalyst, and the initial insertions of the monomer to produce the polymeric entity containing the catalyst incorporating a dye.

When used with initiator **4**, compound **1** efficiently polymerizes L-lactide to yield yellow PLA. The polymer was characterized by differential scanning calorimetry and gel permeation chromatography, and exhibited a molecular weight range of $M_w = 170000$–340000 with a polydispersity index (PDI) of 1.2–1.6 ($M_n = 140000$–300000), and a melting point range of 171–179 °C. These values compare favorably to those obtained for an undyed commercial PLA, wherein the melting temperature is between 160–170 °C for PLA containing only the L- or D-isomeric form.[20]

Compound **1** has been combined with colored initiators to give a range of active catalysts, which in turn have produced a range of different colored polymers, films, and fibers. Examples of DyeCat PLA can be seen in Figure 6. A range of colors has been achieved, and is best demonstrated by the solvent cast films. A yellow DyeCat PLA polymer (Figure 6 a) was synthesized using as the initiator the simple synthetic azo derivative **4** of benzyl alcohol, often used as the initiator in conventional PLA polymerization reactions.[16,17] Commercial dyes are also applicable as initiators; a purple polymer (Figure 6 b) was synthesized using C.I. Disperse Blue 106 **5** and a red polymer (Figure 6 c) was synthesized using C.I. Disperse Red 13 **6**. Figure 6 d shows a DyeCat PLA containing the fluorescent dye 1-pyrenebutanol[21] **7** that was photographed under UV light. The fibers and plastics showed little deterioration in molecular weight or tensile strength during processing. A particularly challenging color to obtain for PLA is black. This is the most widely used color in textile applications, but also the hardest to achieve because of the high dye loadings required, and the tendency for leaching of the dyes from the final product. Figure 6 e shows black melt-spun DyeCat PLA filament, prepared by mixing the yellow and purple polymers (Figures 6 a and b, respectively) in a 1.0:1.8 ratio in the melt-spinning process (220 °C), and subsequently drawing over heated rollers to align the polymer crystallites. The black filament produced was 35.0 tex, had a tensile stress of 52.2 kPa, a Young's modulus of 416.0 $\mathrm{cN\,tex^{-1}}$, a tenacity of 11.9 $\mathrm{cN\,tex^{-1}}$ (see the Supporting Information for a definition of tex), as well as $T_m = 178.1$ °C, and $x_c = 44.4\,\%$, which compare favorably with typical commercial PLA filaments.[20] This black filament has been woven into a black dress which is currently being exhibited in the Science Museum in London (see the Supporting Information).

Samples of the colored PLA filaments were washed according to the ISO (International Organization of Standardization) approved 105:C06/C2 (60 °C) wash test using undyed multifiber as an indicator.[22] There was no reduction in color strength of the PLA and no staining of the multifiber indicator was observed; similarly there was no evidence of any color in the post-wash liquor. From a performance perspective, these colored polymers have greater wash fastness properties with respect to their aqueous-dyed counterparts, presumably because of the covalent bond between the dye and the polymer. As PLA is an aliphatic polymer it has very limited absorbance in the UV range, thereby preventing its application where such absorbance is required. By analogy with the use of visible dyes, a UV absorbing polymer was synthesized using 9-anthracenemethanol **8** as an initiator (absorbance spectrum shown in Supporting Information).

A catalyst typically contains one dye chromophore moiety which yields colorant by mass of 0.5–0.7 % with respect to mass of the polymer; this figure is significantly less than that of similar shades in the conventionally dyed textiles wherein medium and dark shades would typically require 2.0–10.0% dye with respect to the mass of the fiber. Additionally, by incorporating the dye molecule at the polymer synthesis stage the colorant is homogenous throughout the cross-section of the fiber, and results in higher color strength compared to those of fibers dyed using the aqueous exhaustion method, wherein adsorption and diffusion mechanisms do not necessarily yield complete dye homogeneity through the fiber cross-section. This difference is shown in Figure 7 where distribution of color through DyeCat PLA (Figure 7a) is homogenous, and that for a conventionally dyed PLA fiber (Figure 7b) is nonhomogenous and the dye molecules aggregation; this heterogeneity often leads to the phenomenon known as "ring dyeing", which results in an observed reduction in color strength.[23–26] In general, homogenous distribution of the dye through the cross-section of a fiber tends to yield higher K/S (Ratio of absorption to scattering, a measure of the visual color strength) values in comparison with those for fibers in which the dye is primarily located at the periphery.[23–26] Therefore, the color strength of DyeCat polymers will be in excess of those obtained through conventional dyeing processes, allowing lower dye levels to be used and no waste typical of a conventional dyeing procedure.

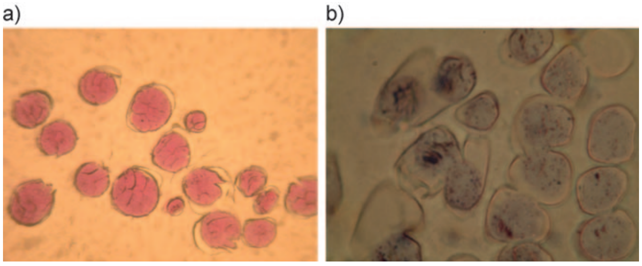


Figure 7. Optical microscopy images of the cross-sections through a) a DyeCat PLA sample, b) a sample of commercially available PLA fiber that was dyed using a conventional method involving a disperse dyeing process.

PLA will become increasingly important as a sustainable polymer through the 21st century and its increasing use will ease the strain on fossil fuel resources and decrease atmospheric carbon dioxide levels. The catalytic process presented herein represents a significant step forward in green chemistry and overall efficiency in terms of completely eliminating the fiber wet-processing stages in the PLA supply chain. There are environmental advantages over the current practices of fiber preparation, dyeing, and finishing, as it decreases the water consumption and energy required to heat water. There is no waste dye and no subsequent effluent treatment of colored waste water. The approach of combining the coloration process with polymer synthesis overcomes the current shortcomings of aqueous dyed PLA (and other polymers), reduces the cost of PLA processing, and fulfills all the technical requirements for apparel and related uses to afford an economic, sustainable, and feasible replacement for standard polyesters.

Received: August 6, 2010

Keywords: aluminum · dyes/pigments · polymers · synthetic methods · textiles

---

[1] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484.
[2] C. E. Lowe, U.S. Patent 2668162, (E. I. du Pont de Nemours & Co.), **1954**.
[3] R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater.* **2000**, *12*, 1841.
[4] R. A. Gross, B. Kalra, *Science* **2002**, *297*, 803.
[5] H. Tsuji, Y. Ikada, *J. Polym. Sci. Part A* **1998**, 36, 59.
[6] www.ingeofibers.com/ingeo/home.asp.
[7] D. Mecerreyes, R. Jerome, *Macromol. Chem. Phys.* **1999**, *200*, 2581.
[8] S. M. Burkinshaw, *Chemical Principles of Synthetic Fibre Dyeing*, Chapman and Hall, London, **1995**.
[9] R. S. Blackburn, X. Zhao, D. W. Farrington, L. Johnson, *Dyes Pigm.* **2006**, *70*, 251.
[10] A. D. Cunningham, *Text. Chem. Color.* **1996**, *28*, 23.
[11] R. S. Blackburn, A. Harvey, *Environ. Sci. Technol.* **2004**, *38*, 4034.
[12] R. O. Alves de Lima, A. P. Bazo, D. M. F. Salvadori, C. M. Rech, D. d. P. Oliveira, G. d. A. Umbuzeiro, *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* **2007**, *626*, 53.
[13] D. P. Oliveira, P. A. Carneiro, C. M. Rech, M. V. B. Zanoni, L. D. Claxton, G. A. Umbuzeiro, *Environ. Sci. Technol.* **2006**, *40*, 6682.
[14] Y. Shen, H. Tang, S. Ding, *Prog. Polym. Sci.* **2004**, *29*, 1053.
[15] D. G. Timms, (Enichem Elastomers Ltd., UK). Application: EP 312213, **1989**, p. 6.
[16] P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2004**, *126*, 2688.
[17] Y.-C. Liu, B.-T. Ko, C.-C. Lin, *Macromolecules* **2001**, *34*, 6196.
[18] L. E. Breyfogle, C. K. Williams, V. G. Young, M. A. Hillmyer, W. B. Tolman, *Dalton Trans.* **2006**, 928.
[19] C. K. Williams, N. R. Brooks, M. A. Hillmyer, W. B. Tolman, *Chem. Commun.* **2002**, 2132.
[20] D. W. Farrington, J. Lunt, S. Davies, R. S. Blackburn, in *Biodegradable and Sustainable Fibres* (Ed.: R. S. Blackburn), Woodhead Publishing, Cambridge, **2005**, pp. 191.
[21] C. A. Nguyen, E. Allemann, G. Schwach, E. Doelker, R. Gurny, *Eur. J. Pharm. Sci.* **2003**, *20*, 217.
[22] *Standard methods for the determination of the colorfastness of textiles and leather*, 5th ed., Society of Dyes and Colourists, **1992**.
[23] E. H. Allen, G. Goldfinger, *J. Appl. Polym. Sci.* **1972**, *16*, 2973.
[24] E. H. Allen, G. Goldfinger, *J. Appl. Polym. Sci.* **1973**, *17*, 1627.
[25] T. L. Dawson, J. C. Todd, *J. Soc. Dyers Colour.* **1979**, 95, 417.
[26] D. A. Garrett, R. H. Peters, *J. Text. Inst.* **1956**, *47*, T166.