Homo- and Copolymers of Furan–Maleic Anhydride and Furan–Dimethylacetylene Dicarboxylate Adducts via Aqueous Ring-Opening Metathesis Polymerization

TITO VISWANATHAN,* JAGDISH JETHMALANI, and ALAN TOLAND

Department of Chemistry, University of Arkansas at Little Rock, Little Rock, Arkansas 72204

SYNOPSIS

Homo- and copolymers of the Diels–Alder adduct of furan with maleic anhydride (F–MA) and of furan with dimethylacetylene dicarboxylate (F–DMAD) were synthesized by aqueous ring-opening metathesis polymerization and characterized by IR, NMR, and DSC. Microstructural product analyses by ^{13}C-NMR indicated the copolymer composition to be 50 : 50 of each of the monomers when an equimolar mixture of RuCl$_3$ and K$_2$RuCl$_5$ was used as the catalyst, with the cis-form predominant for poly(F–MA) and the trans-form predominant for poly(F–DMAD). On the practical side, the acidic and ester functionality of the copolymer would lend itself to be both blendable (and selectively extractable) with some already existing *petroleum-based acrylate* polymers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Novel polymers using furan—a renewable resource that can replace or modify existing petroleum-based products, would decrease our reliance on the non-renewable energy resource. Coincidentally, the newly discovered aqueous ring-opening metathesis polymerization (ROMP) of 7-oxanorbornene systems provides an economical way to synthesize high molecular weight polymers using a recyclable transition-metal catalyst. Even though a living system is not obtained in these cases, the molecular weights are as high as 10^6 or more with a polydispersity close to 1.[1] In the first instance, it would seem that a countless number of furan-based polymers could be made. However, further reflection would prove this optimism to be illusory. The 7-oxanorbornene systems prepared by the Diels–Alder adduct of furan are notoriously slow and, in most cases, do not occur even with excellent dienophiles. Only a handful of these reactions occur in high yields to be deemed economically useful. Two such reactions that can also impart useful property due to functional groups

present in them include the Diels–Alder adduct of furan with maleic anhydride (F–MA) and of furan with dimethylacetylene dicarboxylate (F–DMAD).

Of unrelated significance are copolymers of methacrylic acid and ethyl acrylate that are already being used in disposable packaging material in Europe.[2] This polymer has the advantage of being compatible with nonpolar materials and yet is extractable by base. This is a distinct advantage in purification that is usually associated with recycling polymers. The polymer dissolved in base may be reprecipitated by addition of dilute HCl.

Copolymer prepared in this project (Fig. 1) would exhibit similar characteristics due to the associated functionality. The reactivity ratios of the two monomers is also important to determine the ratio of acid to ester. Higher acid content increases the solubility of the polymer in polar solvents. The ester/acid ratio should also affect other properties such as T_g, melt index, tensile strength, elongation, and modulus.

EXPERIMENTAL

^{1}H- and ^{13}C-NMR spectra were recorded on a Brüker AC-F 200 MHz (50 MHz ^{13}C) instrument. Chemical shifts are referenced to residual protons on deuter-
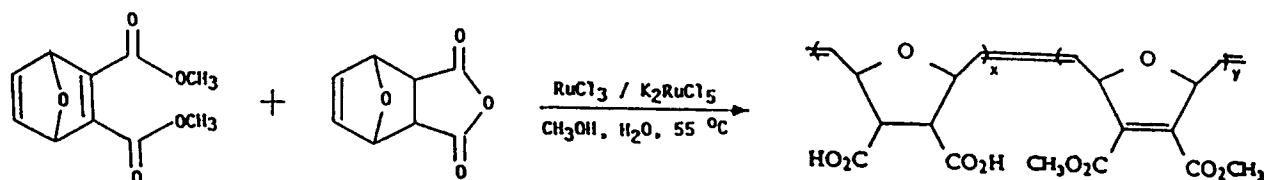

Figure 1 Preparation of poly(F-MA-co-F-DMAD) by aqueous ROMP.

ated solvents. IR spectra were acquired on a Perkin-Elmer ratio recording spectrometer using a 1730 computer data station. Samples were spread on NaCl plates. Thermal analysis was performed on a Mettler DSC-20 with a scan rate of $10°C/min$.

All reagents except K_2RuCl_5 were purchased from the Aldrich Chemical Co., Milwaukee, WI. Maleic anhydride was recrystallized from $CHCl_3$ prior to use. K_2RuCl_5 was purchased from Johnson-Matthey/AESAR.

Monomer Synthesis

The synthesis of F-MA was accomplished by reacting furan with maleic anhydride according to a previously published procedure.[3] The *exo* configuration was confirmed by ^1H-NMR data according to Lee and Herndon.[4] ^{13}C-NMR shift values ($CDCl_3$ solvent) were 169.9 ppm for carbonyl carbons, 137 ppm for olefinic carbons, 82.2 ppm for allylic carbons, and 48.7 ppm for methine carbons.

The synthesis of F-DMAD was accomplished by reacting furan with dimethylacetylene dicarboxylate according to a previously published procedure[5] and purified by flash chromatography on silica gel using 10% ethyl acetate/90% benzene as solvent. The ^{13}C-NMR shift values ($CDCl_3$ solvent) were 163.3 ppm for carbonyl carbon, 153 ppm for C-2 and C-3, and 143.3 ppm for C-5 and C-6, 85.1 ppm for C-1 and C-4, and 52.4 ppm for the CH_3 carbons. Because of the adduct instability to heat, the monomer was used as soon as the pure sample was prepared.

Polymer Synthesis

Homopolymerization of F-DMAD was carried out in 90% MeOH/10% deionized degassed H_2O and in 100% deionized degassed H_2O for F-MA at 55°C for varied amounts of time. The concentration of the monomer varied between 1.4 and $1.7M$. The catalyst (either K_2RuCl_5 or $RuCl_3$) was kept at 5% (mole basis) of the monomer used. The crude F-DMAD polymer precipitate was purified by reprecipitation from a nonsolvent (CH_3OH).

Purification of the polymer derived from the F-MA adduct was achieved by addition of $1M$ HCl, dissolution in 2% NaOH, and reprecipitation by addition of $1M$ HCl. The polymer was then washed with water and dried under vacuum at room temperature.

The copolymer of F-MA and F-DMAD was prepared as follows: F-DMAD, 0.6325 g (0.003 mol) and F-MA, 0.5 g (0.003 mol) were mixed together and to this was added 3.69 mL of CH_3OH and 0.41 mL of degassed deionized H_2O. $RuCl_3$ 0.312 g (1.5 $\times 10^{-4}$ mol) and K_2RuCl_5, 0.0592 g (1.5 $\times 10^{-4}$ mol) were also added to the mixture and stirred. The resulting solution was heated in a water bath at 55°C for 6 h. The polymer that formed precipitated out of solution. Dissolution of the polymer was attempted several times in CH_3OH (to dissolve any F-MA homopolymer) and then several times in $CHCl_3$ (to dissolve any F-DMAD homopolymer) and the remaining product was dried prior to spectroscopic characterization. No decrease in weight after the treatment suggested absence of or insignificant (discreet) homopolymer formation during the polymerization.

RESULTS AND DISCUSSION

We have found that although K_2RuCl_5 is able to polymerize F-MA readily, it is very slow, at best, at polymerizing F-DMAD. In contrast, although $RuCl_3$ can polymerize F-DMAD, it is unable to polymerize F-MA even after a 24 h incubation period. Furthermore, K_2RuCl_5 alone is extremely slow in initiating copolymerization of F-MA/F-DMAD and the yield obtained is poor. Product yield with $RuCl_3$ was slightly better than with K_2RuCl_5, probably because the "activated Ru^{2+}" formed by polymerizing F-DMAD also polymerizes F-MA. However, we have found that an equimolar mixture of $RuCl_3$ and K_2RuCl_5 is able to initiate copolymerization much more readily and yields of the copolymer are relatively high (40%).

The reason behind the differential catalytic behavior of $RuCl_3$ and K_2RuCl_5 in aqueous ROMP of
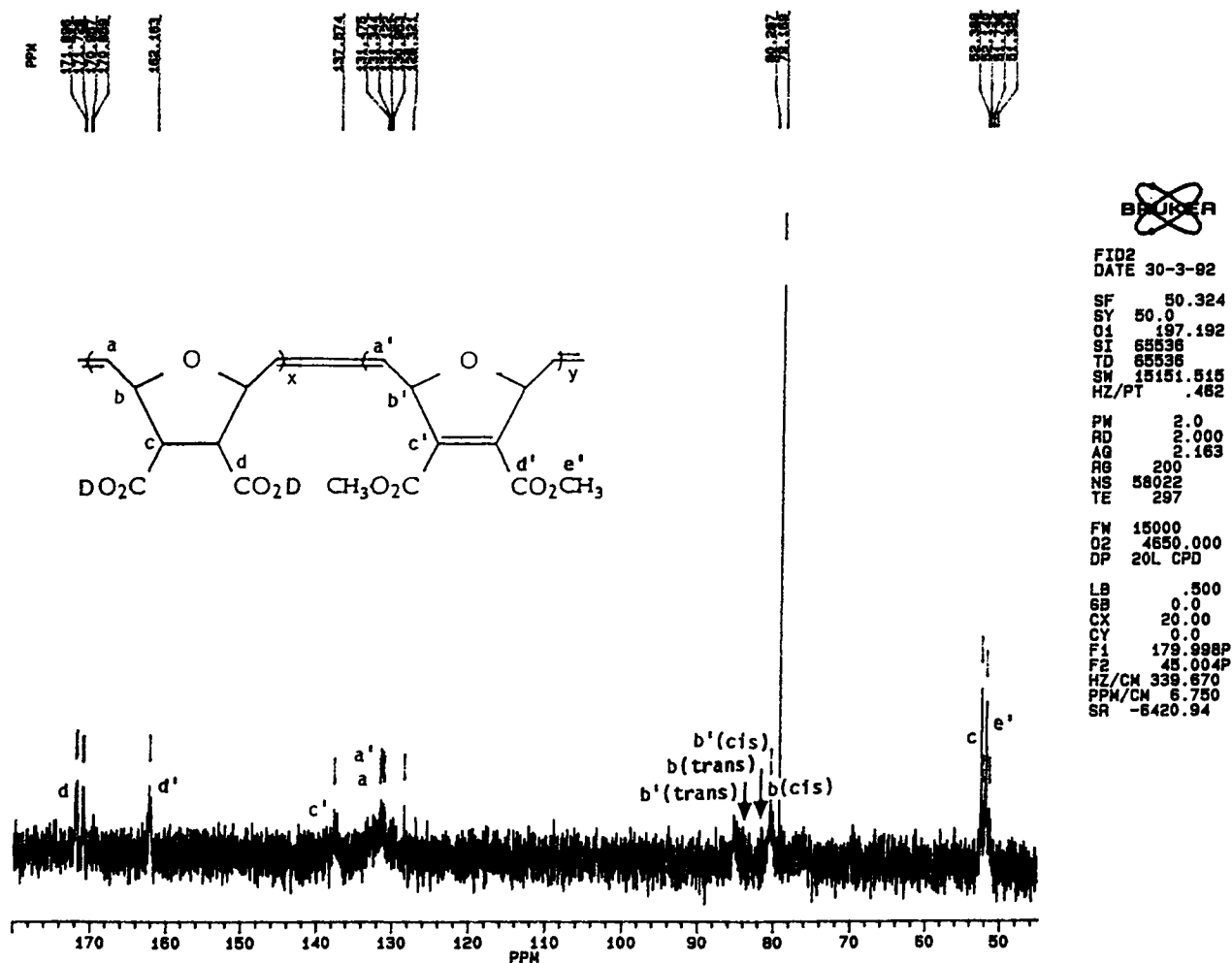
Figure 2 ^{13}C-NMR spectrum of poly(F-MA-*co*-F-DMAD) prepared using a 50 : 50 mixture of RuCl$_3$ and K$_2$RuCl$_5$ (DMSO-d_6 solvent).

F-MA and F-DMAD has been discussed earlier.[6] We had concluded that whereas the ruthenium in RuCl$_3$ complexes with the C5 — C6 double bond in F-DMAD that in K$_2$RuCl$_5$ complexes with the C2 — C3 end and is deactivated. Also, RuCl$_3$ is deactivated by F-MA, whereas K$_2$RuCl$_5$ polymerizes F-MA by complexing with the C5 — C6 end.

Figure 2 shows the ^{13}C-NMR of the copolymer of F-MA and F-DMAD prepared using a 50 : 50 mixture of RuCl$_3$ and K$_2$RuCl$_5$. (The ^{1}H-NMR is much too complicated for easy analysis.) The copolymer carbon spectrum is relatively simple and gives peaks as expected. Peak assignments at shifts higher than 120 ppm are easily explained and are shown in the figure. Peaks due to allylic carbons are found to be between 75 and 90 ppm. The ^{13}C- and ^{1}H-NMR of the homopolymers of F-MA and F-DMAD exhibit a predominance of *cis*-isomer in the case of the

former and *trans*- in the case of latter and the peak at 85.0 ppm corresponds to the (*trans*) allylic carbon for the F-DMAD unit. The *cis*-form is negligible and does not show up significantly. The peak at 80.29 ppm corresponds to the (*cis*) allylic carbon of the F-MA unit. This resonance position overlaps with the (*cis*) allylic of the F-DMAD unit. The very small peak at 83.5 ppm corresponds to the (*trans*) allylic carbon of the F-MA unit.

Finally, the peaks between 52.39 and 51.34 ppm are due to the CH$_3$ — of F-DMAD and the methine carbon of the F-MA unit. We thus conclude that the composition of the copolymer of F-MA and F-DMAD is approximately 50% each, with the *trans*-form predominating for the F-DMAD unit and the *cis*-form predominating for the F-MA unit. We are unable to explain the peak observed at 79.17 ppm at this point and it is probably due an impurity.

The IR of the copolymer seems to be a composite of the IR of the homopolymers, even though it is not worthy of extended discussion. The DSC of the copolymer shows two major exotherms close to each other, one at 370°C and the other at 415°C. The DSC of the F–DMAD homopolymer shows an exotherm at 460°C, and the F–MA polymer exhibits one at 470°C. Analysis after heating the polymers above the exotherm temperature shows that the polymers are degraded/cross-linked as indicated by their insolubility in all solvents tested.

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