Synthesis and Characterization of New Comb-shape Copolymers Based on 3,5-Isoxazolines.

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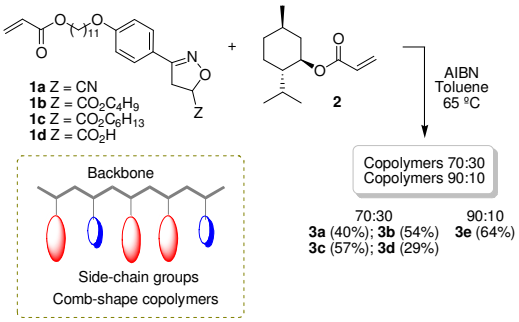
INTRODUCTION

Copolymerization is one of the important techniques adopted in effecting systematic changes in the properties of commercially important polymers[1]. It is possible to tune the polymer taking advantages from the monomers for especial application improving the characteristics of polymer turning it more interesting commercial and for technology applications[2].

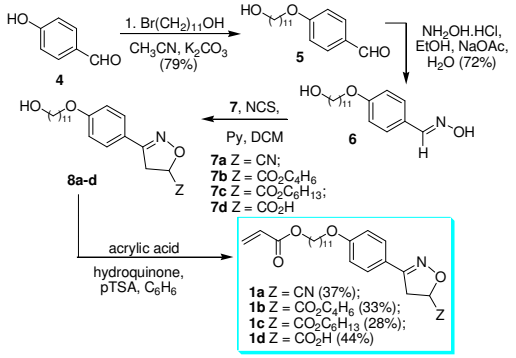
RESULTS AND DISCUSSION

In this work we prepared new comb-shape polyacrylates copolymers **3a-e** through radical polymerization as outlined in Scheme 1. The copolymers are comprised of monomer **1a-d** and **2**.



Scheme 1. Synthesis of comb-shape copolymers **3a-e.**

The preparation of the monomers[3] **1a-d** (Scheme 2) began with the alkylation of aldehyde **4** with 11-bromo-1-undecanol ($MeCN/K_2CO_3$) to gave **5**, followed by oximation reaction to yield the corresponding oxime **6** in a good yields.



Scheme 2. Synthesis of the monomers **1a-d.**

The next step was to synthesize **8a-d** using the cycloaddition [3+2] 1,3-dipolar between aryl nitrile oxide derived from **6** and dipolarophiles **7a-d**. The oxime **6** was reacted with the dipolarophiles **7a-d** in the presence of *N*-chlorosuccinimide, pyridine in dichloromethane. **8a-d** were obtained in 61%-89% yields. The monomers **1a-d** were prepared through esterification between the isoxazoline **8a-d** and acrylic acid with low yields after 28%-44% yield.

The chiral monomer **2** was prepared by coupling between (-)-menthol and acrylic acid in 65% yield. The copolymers **3a-d** were prepared in molar proportion between the monomers **1a-d** and the monomer **2** in 70:30 and the copolymer **3e** with the monomer **1c** and the monomer **2** in a molar proportion of 90:10.

The copolymers were analyzed with GPC, DSC and the molar proportion was confirmed with NMR ^1H analysis (Table 1).

Table 1: GPC and DSC data of copolymers **3a-e**.[a]

Copolymers	Tg (°C)	Mn	Mw	PD
3a	0	6,429	8,148	1.27
3b	0	10,153	18,372	1.81
3c	16.2	12,800	18,508	1.45
3d	27.5	13,239	24,201	1.83
3e	-10.0	8,836	10,500	1.18

[a]Tg: glass transition temperature; Mn: number-average molecular weight; Mw: weight-average molecular weight; PD: polydispersity.

The DSC analysis showed that the copolymers **3a-e** are amorphous with Tg between -10°C and 27.5°C. The Mn copolymers **3a-e** are in the range of 6,429 – 13,239 daltons. No mesomorphic behavior was observed for all samples.

CONCLUSION

Comb-shape Polyacrylates copolymers with side chains **3a-e** were synthesized and characterized. The copolymers are amorphous with low glass temperature transition.

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