DEVELOPMENT OF NEW FUMARAMIDE GELATORS AND TRANSCRIPTION GELS IN POLYMERS

Tomislav Gregorić and Leo Frkanec

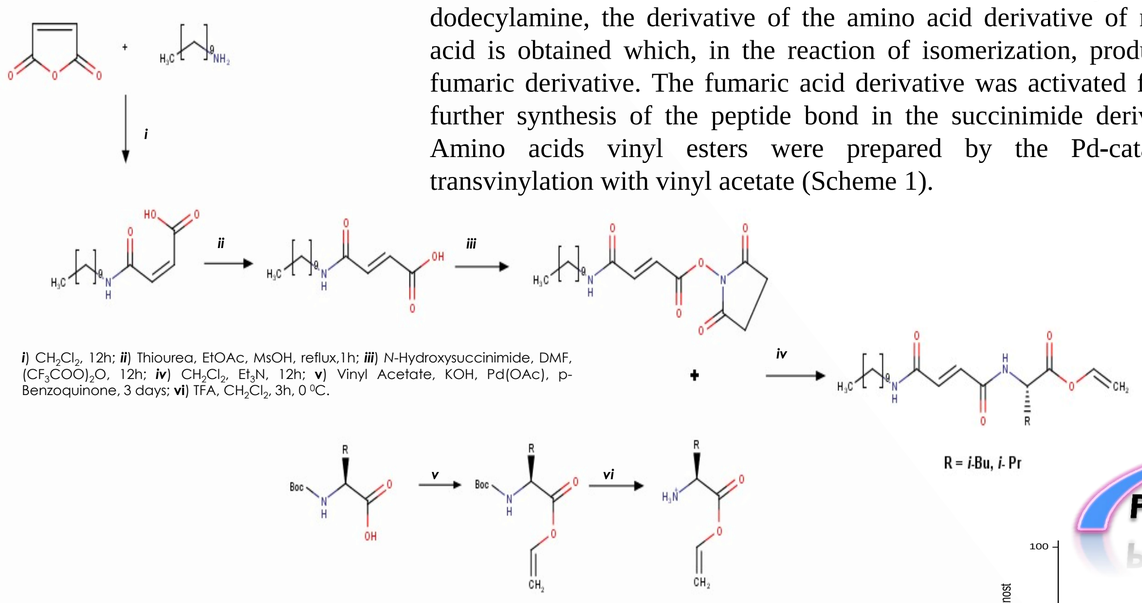
Laboratory of Supramolecular Chemistry, Division of Organic Chemistry and Biochemistry,
Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia,
E-mail: tgregor@irb.hr

INTRODUCTION

A major challenge in supramolecular chemistry is the synthesis of new materials that have improved properties for various uses in medical science, development of new biomaterials, sensors and many others[1]. Supramolecular chemistry has found interest in the synthesis of new materials because it provides a wide range of possibilities for generating new materials as self-organized nanomaterials using non-covalent interactions such as hydrogen bonds, π–π stacking or Van der Waals forces. We have investigated the synthesis of new polymers[2]. For this purpose have developed new amino acid vinyl fumaric acid derivatives such as mono(vinyl-amino acid) fumaramide. The novel supramolecular low molecular weight gelator is obtained. These compounds are capable of forming gels with various organic solvent. We investigated the possibility of polymerization in gels induced by UV rays. The polymerization only occurred in acetonitrile gel, we have shown that small changes in the structure of compound cause specific self-organization through non-covalent interactions which effects on the reactivity of crosslinked molecules. The resulting self-assembles in different solvents are characterized by ^{1}H, ^{13}C, temperature dependent NMR and FTIR spectroscopy. Morphology of gel network and polymers are determined by TEM, SEM and AFM microscopy.

SYNTHESIS

The first step in synthesis of compounds was to prepare a vinyl ester of valine fumaric-dodecilamine. In the reaction of maleic anhydride and dodecylamine, the derivative of the amino acid derivative of maleic acid is obtained which, in the reaction of isomerization, produces a fumaric derivative. The fumaric acid derivative was activated for the further synthesis of the peptide bond in the succinimide derivative. Amino acids vinyl esters were prepared by the Pd-catalyzed transvinylation with vinyl acetate (Scheme 1).



i) CH_2Cl_2, 12h; ***ii***) Thiourea, EtOAc, MsOH, reflux,1h; ***iii***) *N*-Hydroxysuccinimide, DMF, $(CF_3COO)_2O$, 12h; ***iv***) CH_2Cl_2, Et_3N, 12h; **v**) Vinyl Acetate, KOH, Pd(OAc), p-Benzoquinone, 3 days; **vi**) TFA, CH_2Cl_2, 3h, 0 °C.

Scheme 1. Synthesis of compounds**.**

GEL CHARACTERIZATION

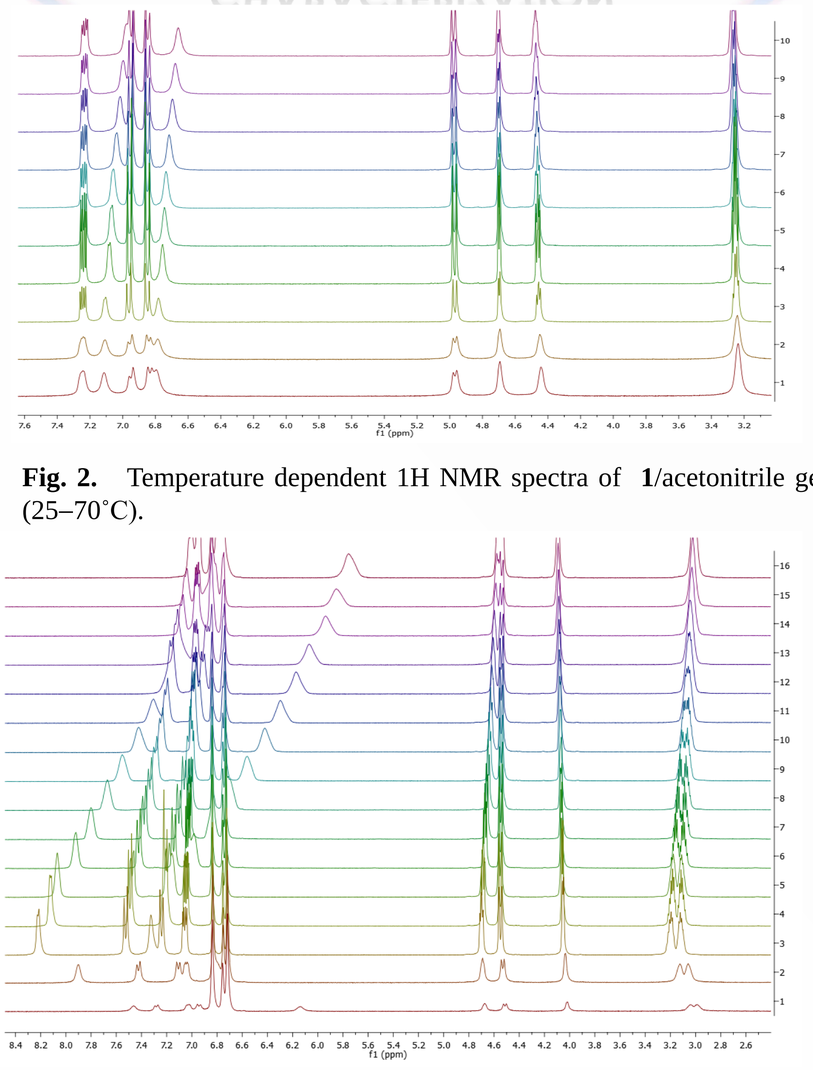


Fig. 2. Temperature dependent 1H NMR spectra of **1**/acetonitrile gel (25–70˚C).

Fig. 5. Temperature dependent 1H NMR spectra of **1**/toluene gel (25–100˚C).

Table 1. Gelation of various solvents by 10 mg of compounds. The result is expressed as the maximal volume of gelled solvent V_{max} / mL

Solvents	1 (*i*–Pr)	2 (*i*–Bu)
H_2O	not soluble	not soluble
H_2O/DMSO	0.77:1.28	0.75:1.21
H_2O/DMF	1.22:0.81	0.79:0.94
EtOH	solution	solution
±2-Octanol	solution	solution
THF	solution	solution
Dioxane	solution	solution
Acetone	solution	solution
EtOAc	precipitate	precipitate
CH_2Cl_2	solution	solution
CH_3CN	0.93+1.05 UZ	0.52+1.05 UZ
Toluene	0.93 (after 3h)	0.43 (after 4h)

GEL POLYMERIZATION

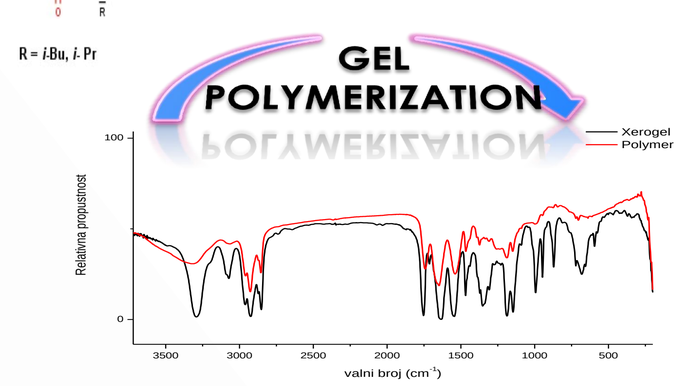


Fig. 1. Temperature dependent FTIR spectra of compound**1**/acetonitrile xerogel (black) and obtain polymer withe the UV-rays (red).

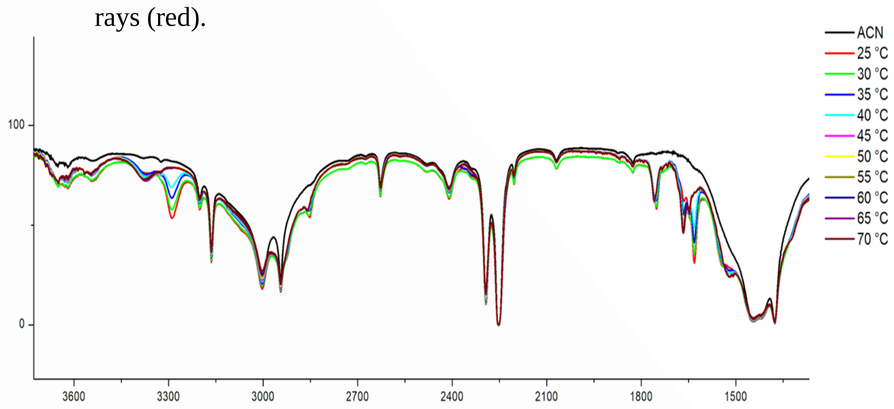


Fig. 3. Temperature dependent FTIR spectra of compound **1**/acetonitrile gel.

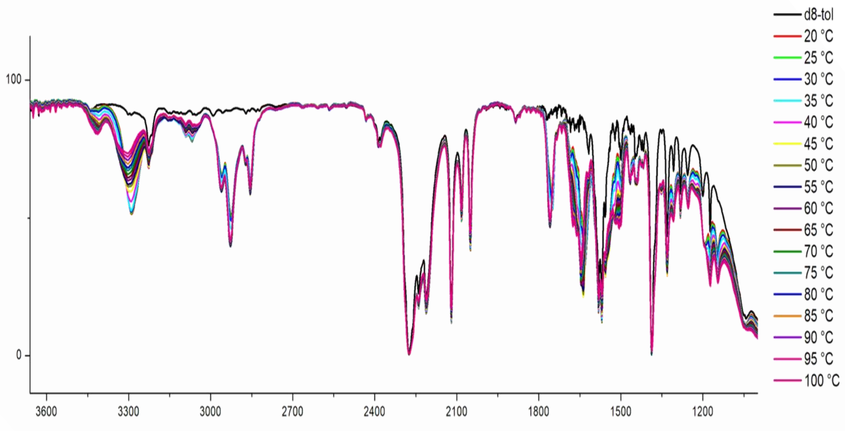
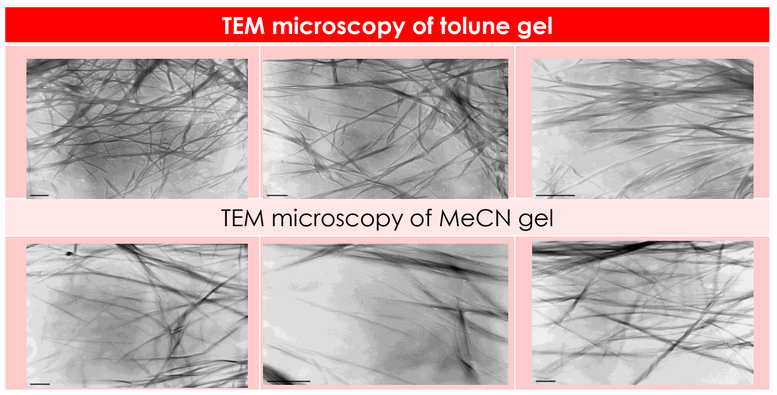
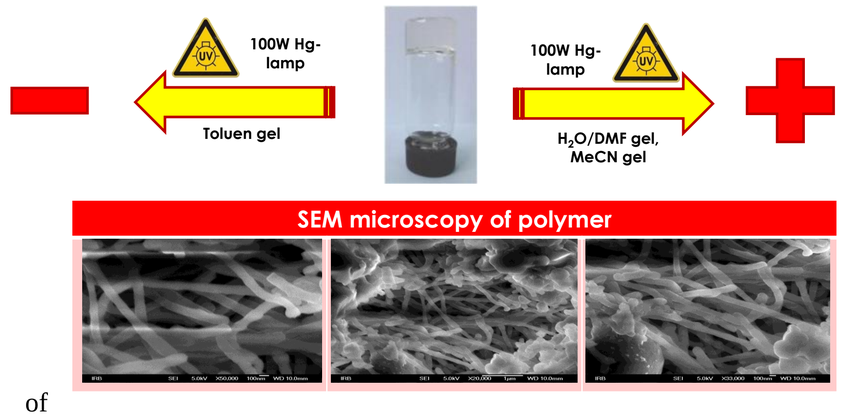


Fig. 6. Temperature dependent FTIR spectra of compound **1**/toluene gel.

TEM & SEM MICROSCOPY





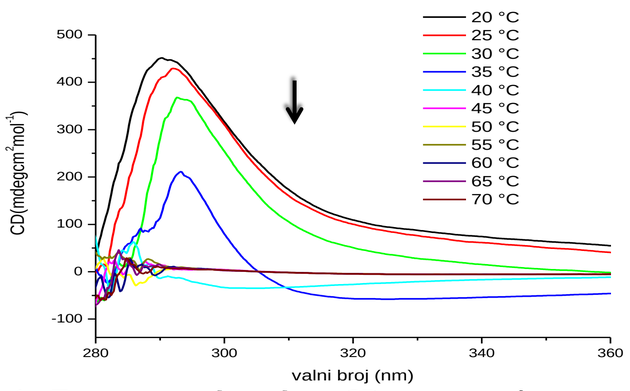


Fig. 4. Temperature dependent CD spectra of compound **1**/ acetonitrile gel.

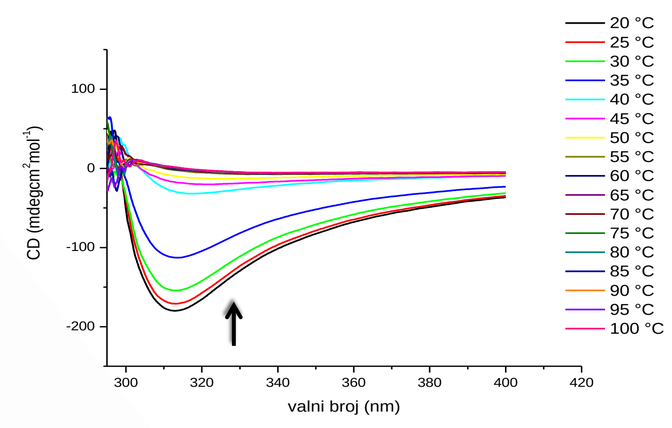
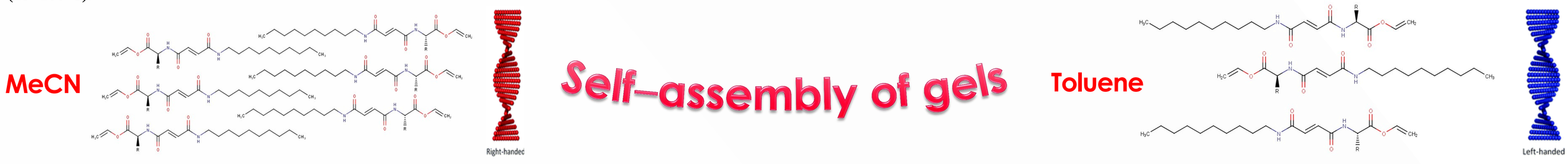


Fig. 7. Temperature dependent CD spectra of compound **1**/ toluen gel.



CONCLUSION

Synthesized compound **1** and **2** is a supramolecular gelator of several organic solvents. We have investigated the self-assemby in gel by various spectroscopic techniques such as NMR, FTIR, CD spectroscopy. We can notice the difference in self-assemby gels of compounds in various solvents (toluene and acetonitrile) which leading to differences in the polymerization reactions.

We greatly appreciate the financial support of the Croatian Science Foundation, projects No. HRZZ-IP-2018-01-6910.

1 E. Busseron, Y. Ruff, E. Moulin, N. Giuseppone, Nanoscale, 2013, 5, 7098.
2 D. J. Cornwell and D. K. Smith, Mater. Horiz., 2015, 2, 279.
3. G. Liu , J. Sheng, H. Wu, C. Yang, G. Yang, Y. Li, R. Ganguly, L. Zhu and Y. Zhao, J. Am. Chem. Soc., 140 (2018) 6467.