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Synthesis and Radical Polymerization of 2-Vinylcyclopropanes

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SUMMARY: The radical polymerization of 1,1-disubstituted 2-vinylcyclopropanes with electron-withdrawing substituents results in polymers with mainly 1,5-ring-opened units. Moreover, they show a significant lower volume shrinkage during their ring-opening polymerization than other vinyl monomers, such as methacrylates. New asymmetric 1,1-disubstituted 2-vinylcyclopropanes were synthesized and polymerized. Hybrid 2-vinylcyclopropanes were polymerized step-by-step under the formation of reactive polymers and polymer networks. Multifunctional cross-linking vinylcyclopropanes were used as new low-shrinking matrix monomers for photopolymerizable materials. In addition, the sol-gel process of trialkoxysilyl-functionalized 2-vinylcyclopropanes afforded low shrinking organic-inorganic nanocomposites.

Introduction

Cyclic monomers, such as spiro orthocarbonates, spiro orthoesters, cyclic acrylates or cyclic ketene acetals, may show a near zero volume shrinkage or some times expansion in volume during their ring-opening polymerization, therefore, are of interest in the fields of precision castings, composites or adhesives1). Unfortunately, the application of these cyclic monomers was frequently accompanied by fundamental problems:

1. Cyclic monomers, for example, methylene-substituted spiro orthocarbonates2), were often not very stable and besides sensitive to water, glass fillers or acidic impurities.
2. The ring-opening tendency of these cyclic monomers depends on the mode of initiation and the polymerization conditions. For example, in the radical polymerization of 2-methylene-1,3-dioxepanes3) the ring-opening mechanism is predominant, whereas under cationic conditions, vinyl-type polymers are formed. Moreover, in case of the radical polymerization of cyclic ketene acetals, the content

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of the ring-opened units of the formed polymers increases with the polymerization temperature.

3. As a result of the ring-opening polymerization, polymers are formed, which partially show poor mechanical properties and insufficient stability. For instance, the radical ring-opening polymerization of 2-methylene-1,3-dioxepanes(3) yields aliphatic polyester and their chain flexibility compromises the mechanical properties of composites based on this substance. As another example, the radical ring-opening polymerization of 2-aryl-methylene-1,3-dioxolan-4-ones results in polymer backbones with α-keto-ester units(4,5), which demonstrate less stability against UV-light.

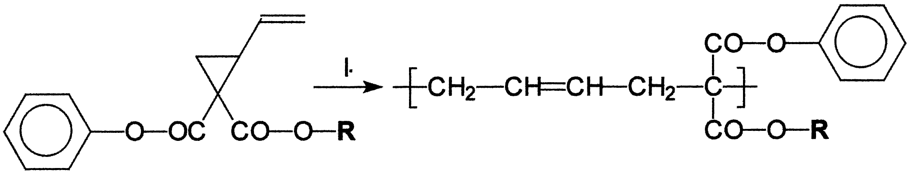
These problems can be widely overcome by 2-vinylcyclopropane (VCP) derivatives. 1,1-Disubstituted VCPs with radical stabilizing and electron-withdrawing substituents have been known as monomers, which undergo radical ring-opening polymerization to result in amorphous polymers bearing mainly a 1,5-ring-opened unit. Therefore, the VCPs show a lower volume shrinkage than linear vinyl monomers(6-11). This paper summarizes our results of the synthesis and radical polymerization of asymmetric 1,1-disubstituted, spirocyclic, hybrid, cross-linking and functionalized VCPs.

1,1-Disubstituted 2-Vinylcyclopropanes

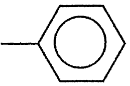
Asymmetric 1,1-disubstituted 1-phenoxycarbonyl-2-vinylcyclopropanes **1a**-**d** were prepared either by the esterification of the corresponding 1-alkoxycarbonyl-2-vinyl-cyclopropane-1-carboxylic acid with phenol, or by the reaction of asymmetric malonates with trans-1,4-dibromo-2-butene(12). The radical polymerization of the asymmetric substituted VCPs in bulk with AIBN results in transparent polymers with ring-opened 1,5-units (*Scheme 1*). The glass transition temperature of the formed polymers varies between 41 and 61 °C.

Furthermore, we also synthesized VCP-s with a spirocyclic or bicyclic structure (*Scheme 2*)(13). The spirocyclic monomers **1e** and **1f** were synthesized by acetalization of 2-vinylcyclopropane-1,1-dicarboxylic acid with 2- or 3-pentanone. The bulk polymerization of monomers **1e**-**h** was carried out in the presence of AIBN (2.5 mol-%) at 65 °C for 15 h. In case of the monomers **1e** and **1g**, the polymerization resulted in solids, which were insoluble in common organic solvents. The monomer

Scheme 1:

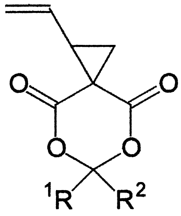


1a-d

1	**a**	**b**	**c**	**d**
R	CH_3	C_2H_5	$CH(CH_3)_2$	CH_2 
T_G (°C)	61	54	57	41

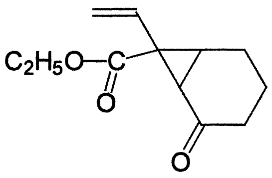
conversion was nearly quantitative. In contrast to this reaction, the polymer yield for the bicyclic monomer **1h** was only about 4%. In case of monomer **1f** (2.0 mol/L), the polymerization in chlorobenzene resulted in well soluble polymers. The polymer yield was about 81 % after a polymerization time of 2 h and the number-average molecular-weight of the formed poly(**1f**) was 113600 g/mol.

Scheme 2:



1e-g

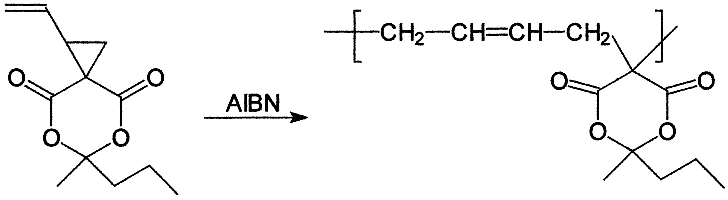
	e	**f**	**g**
R^1	C_2H_5	CH_3	CH_3
R^2	C_2H_5	C_3H_7	CH_3



1h

The ^1H NMR and ^{13}C NMR spectra of the soluble poly(**1b**) clearly indicate the formation of the 1,5-adduct units (*Scheme 3*). Finally, it should be mentioned that also the solid state ^{13}C CP/MAS NMR spectrum of the cross-linked poly(**1c**) was in agreement with the expected ring-opened structure.

Scheme 3:

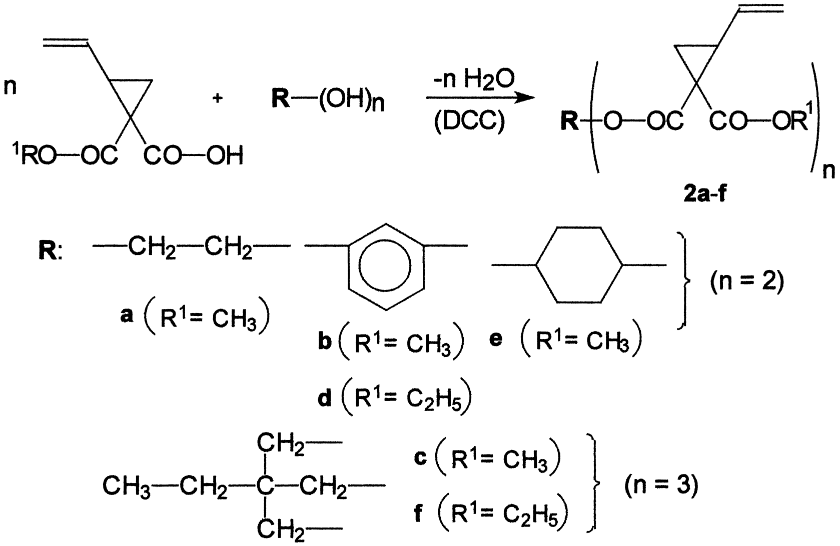


1f poly(**1f**)

Cross-linking 2-Vinylcyclopropanes

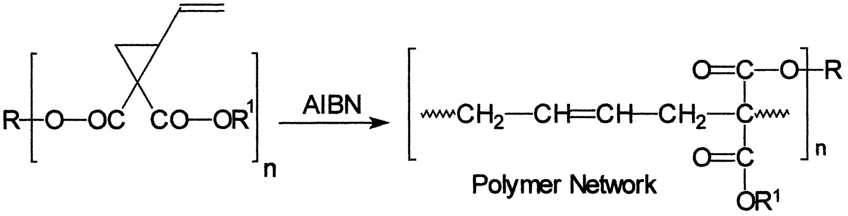
In comparison to monofunctional monomers, cross-linking monomers generally show a higher rate of polymerization. Furthermore, the formed polymers demonstrate improved mechanical properties and a better solvent-resistance. Therefore, we synthesized various bi- and trifunctional VCPs by esterification of 1-alkoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid (R^1 = methyl or ethyl) with ethylene glycol, 1,1,1-trimethylolpropane, 1,4-cyclohexanediol or resorcinol in the presence of 1,3-dicyclohexylcarbodiimide (DCC) (*Scheme 4*)[14,15]. The bulk polymerization of the bi- or trifunctional monomers **2a-f** was carried out in the presence of AIBN and yielded

Scheme 4:



highly transparent solid products. The bulk polymerizates were insoluble in common organic solvents, which confirms the cross-linking properties of the multifunctional VCPs (*Scheme 5*). Furthermore, it was found that the radical polymerization of the liquid VCPs is accompanied by a change in volume of -3.9 (**2c**) to -7.0 % (**2a**), whereas the crystalline monomer **2b** demonstrates an expansion in volume (+1,0 %).

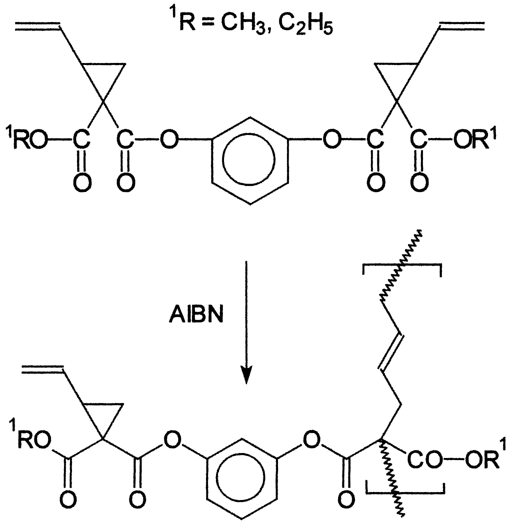
Scheme 5:



In contrast to the bulk polymerization, the polymerization of the cross-linking VCPs **2b** and **2d** in a diluted solution (0.3 M chlorobenzene) resulted in soluble polymers, poly(**2b**) (M_n = 62000 g/mol, T_G = 72 °C) and poly(**2d**) (M_n = 30000 g/mol, T_G = 65 °C) with laterally bonded 2-vinylcyclopropyl groups (*Scheme 6*), which can be cross-linked in a second step.

Furthermore, it should be mentioned that the monomers **2b** and **2d** showed a low

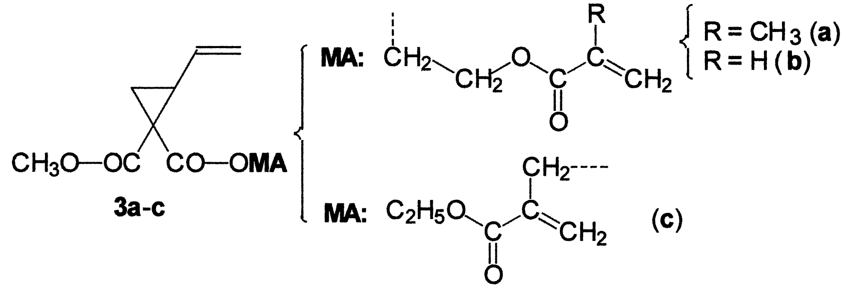
Scheme 6:



oral toxicity (LD_{50} >2000 mg/kg), no mutagenicity and less cytotoxicity than commonly used cross-linking methacrylates. Moreover, the cross-linking VCPs are stable in the presence of humidity, acid, or basic impurities, as well as inorganic fillers, such as silica or glass powder. These properties and the low volume shrinkage during polymerization of the cross-linking VCPs render them attractive as monomer components in dental restorative materials.

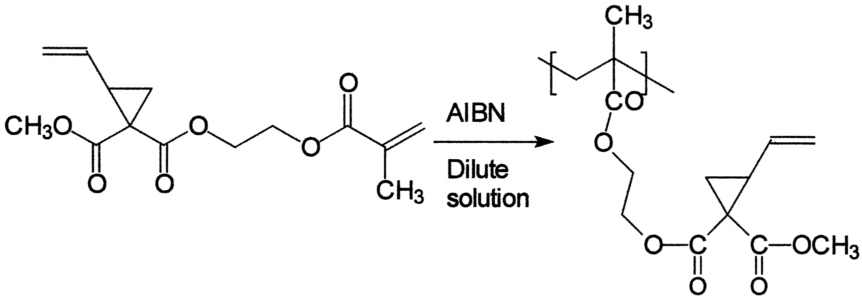
Hybrid monomers **3a-c** (*Scheme 7*) containing both a vinylcyclopropyl and a (meth)-acrylic group were synthesized by the esterification of 1-methoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid with hydroxy group containing methacrylates, such as 2-hydroxyethyl (meth)acrylate or ethyl α-hydroxymethylacrylate16).

Scheme 7:



VCPs are less reactive than methacrylates in the radical copolymerization. Therefore, we were able to polymerize them step-by-step. If these hybrid monomers were radically polymerized in a solution at a relatively low monomer concentration, only the methacrylic groups are involved in the polymerization, and polymers were formed with lateral VCP groups (*Scheme 8*). The formed polymers were dissolved again and

Scheme 8:

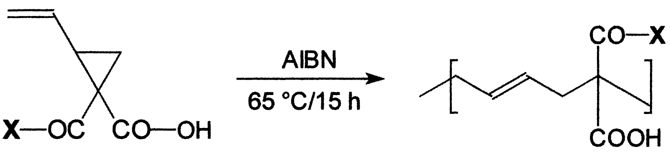


after addition of a radical initiator, these reactive polymers were cross-linked in a second step. Moreover, the gelation occurred faster after the addition of monomers such as methyl methacrylate or 1,1-diethoxycarbonyl-2-vinylcyclopropane.

Functionalized 2-Vinylcyclopropanes

VCP derivatives with reactive functional groups, such as carboxy, acid chloride or trialkoxysilyl groups, enables the preparation of reactive polymers. Thus, the radical polymerization of the 1-alkoxycarbonyl-2-vinylcyclopropane-1-carboxylic acids in dioxane in the presence of AIBN resulted in flexible ring-opened polymers with lateral carboxy groups demonstrating a significantly lower T_G (*Scheme 9*) than, poly(acrylic acid) (T_G = 106 °C).

Scheme 9:



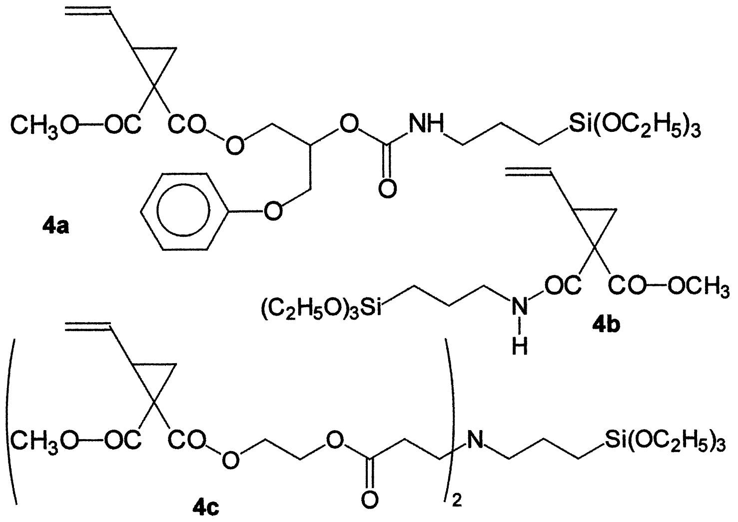
X:	Polymer yield (%)	T_G (°C)
CH_3O	87	50
C_2H_5O	66	37

VCP bearing trialkoxysilyl groups permitted the preparation of inorganic-organic nanocomposites by means of the sol-gel process17). These 2-vinylcyclopropylsilanes **4a-c** (Scheme 10) were synthesized by the reaction of commercially available functionalized silanes, such as 3-isocyanato- or 3-aminopropyltriethoxysilane with suitable VCP derivatives, such as 1-methoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid or its adduct with glycidyl phenyl ether.

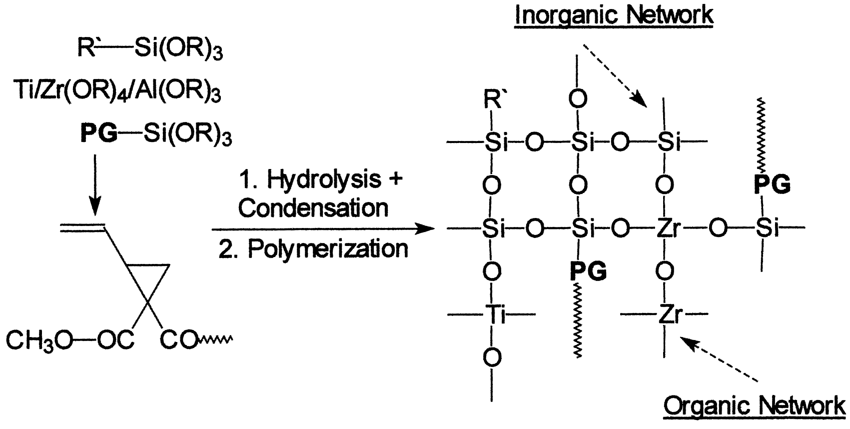
The hydrolysis and condensation of the alkoxy groups as well as the condensation with tetraalkoxysilanes or other metal alkoxides led to homo- or heteropolysiloxanes with lateral VCP groups. Therefore, these solvent-free liquid resins were cured with

UV-light-induced radical polymerization of the VCP groups under the formation of inorganic-organic nanocomposites (*Scheme 11*).

Scheme 10:



Scheme 11:



Conclusion

The radical polymerization of 1,1-disubstituted VCPs with radical stabilizing and electron-withdrawing substituents results in amorphous polymers with predominantly 1,5-ring-opened units. Therefore, the volume shrinkage during polymerization of the

VCPs is significantly lower than the one occurring during the polymerization of linear vinyl monomers, such as methacrylates. In contrast to other ring-opening low-shrinking monomers, such as spiro orthocarbonates or cyclic ketene acetales, the VCPs are stable in the presence of humidity, acid, or basic impurities, as well as inorganic fillers and show a better radical copolymerizability with other vinyl monomers. The radical polymerization of multifunctional VCPs results in transparent, solvent-resistant cross-linked products. In sum these features render the cross-linking VCPs attractive as a new monomer component in low-shrinking adhesives or composites. Hybrid VCPs are polymerized step-by-stepwise under the formation of reactive polymers or polymer networks. In addition, the sol-gel process of trialkoxysilyl-functionalized VCPs afforded low shrinking organic-inorganic nanocomposites.

References

1. R. M. Russel, R., K. Sadhir, Expanding Monomers - Synthesis, Characterization, and Application, CRC Press, Boca Raton 1992, p. 2 ff.
2. N. Moszner, F. Zeuner, V. Rheinberger, *Macromol. Rapid Commun.* **16**, 667 (1995)
3. N. Moszner, T. Völkel, V. Rheinberger, E. Klemm, *Macromol. Chem. Phys.* **198**, 749 (1997)
4. W. J. Bailey, P. Z. Feng, Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem. **28** (1), 154 (1987)
5. N. Moszner, F. Zeuner, V. Rheinberger, *J. prakt. Chem.* **337**, 478 (1995)
6. I. Cho, K.-D. Ahn, J. Polym. Sci., Polym. Lett. Ed. **15,** 751 (1977)
7. I. Cho, K.-D. Ahn, J. Polym. Sci., Polym. Chem. Ed. **17,** 751 (1979)
8. T. Endo, M. Watanabe, K. Suga, T. Yokazawa, Makromol. Chem. **190**, 691 (1989)
9. F. Sanda, T. Takata, T. Endo, Macromolecules **26**, 1818 (1993)
10. J. Sugiyama, K. Ohashi, M. Ueda, Macromolecules **27**, 5543 (1994)
11. N. Moszner, F. Zeuner, V. Rheinberger, *Macromol. Chem. Phys.* **197**, 2745 (1996)
12. N. Moszner, F. Zeuner, U. K. Fischer, V. Rheinberger, *Polymer Bull.* **40**, 447 (1998)
13. N. Moszner, F. Zeuner, J. Angermann, V. Rheinberger, *Polymer Bull.* in press
14. N. Moszner, F. Zeuner, V. Rheinberger, *Macromol. Rapid Commun.* **18**, 775 (1997)
15. N. Moszner, F. Zeuner, T. Völkel, U. K. Fischer, V. Rheinberger, *J. Appl. Polym. Sci.*, in press
16. N. Moszner, T. Völkel, U. K. Fischer, V. Rheinberger, *Macromol. Rapid Commun.* **20**, 33 (1998)
17. S. Stein, N. Moszner, T. Völkel, V. Rheinberger, Mat. Res. Soc. Symp. Proc. **519**, 357 (1998)