Thermodynamic Recycling—On Ring-Opening Polymerization and Ring-Closing Depolymerization

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THERMODYNAMIC RECYCLING—ON RING-OPENING POLYMERIZATION AND RING-CLOSING DEPOLYMERIZATION

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ABSTRACT

The ring-opening polymerization of various cyclic monomers has been extensively investigated in the past, e.g., the cationic polymerization of tetrahydrofuran, the anionic polymerization of ϵ-caprolactone, the metathesis polymerization of cycloalkenes, and the anionic or cationic polymerization of cyclohexamethyltrisiloxane and cyclooctamethyltetrasiloxane. In conjunction with ring-opening polymerization, monomer–polymer equilibrium (ceiling temperature) and/or the formation of a ring–chain equilibrium have also been studied. In the last few years we have studied extensively the anionic ring-opening polymerization and copolymerization of cyclic carbonates, the monomers mostly being provided by depolymerization of the polymers which were obtained by polycondensation polymerization. This fact has led to the development of a new polymer recycling concept by depolymerization and repolymerization, which we call thermodynamic recycling.

INTRODUCTION

In recent years recycling of polymers has become a main subject of discussions, symposia, and scientific work. In general, recycling concepts reach from energetical recycling to materials recycling.

Figure 1 indicates a concept with particular consideration of the formation of
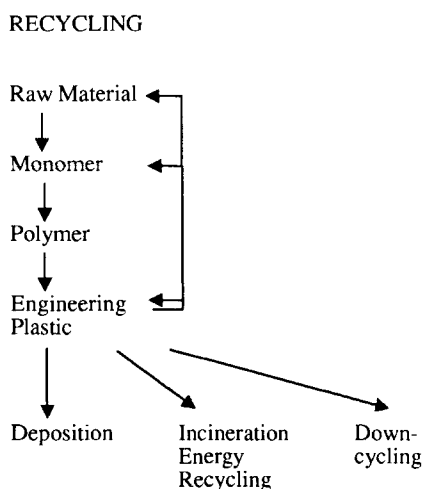
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RECYCLING

FIG. 1.   Recycling scheme.

monomers from polymeric material which can be separated by distillation and are —
in many cases — then ready for polymerization.

This concept is certainly not a general one. It will be shown, however, that it
can be applied successfully to particular polymers and even copolymers.

Polyreactions are usually subdivided into chain growth reactions, initiated
radically, ionically, or by metal organic complexes, and stepwise reactions compris-
ing polycondensation, polycombination, and polyaddition reactions.

All reactions are generally characterized by a thermodynamic equilibrium:

$$P_n + M \rightleftharpoons P_{n+1} \tag{1}$$

This equilibrium is characterized by an equilibrium constant which to a first approx-
imation is equal to the inverse equilibrium monomer concentration:

$$K = [P_{n+1}]/([P_n][M]_e) \approx 1/[M]_e \tag{2}$$

Equation (3) discloses the connection between the equilibrium monomer concentra-
tion and the free enthalpy of polymerization as the driving force of the polymeriza-
tion.

$$\ln [M]_e = \Delta G/RT = \Delta H°/(RT) - \Delta S°/R \tag{3}$$

For standard conditions (initial monomer concentration equal to 1 M) and for
a certain critical temperature, the equilibrium constant may be 1 and hence the
equilibrium monomer concentration is 1 M. Under these conditions, no polymer is
obtained.

From a thermodynamic point of view, the critical temperature is defined as
the ceiling temperature T_c with both ΔH and $\Delta S < 0$ (and as the floor temperature,
T_f for both ΔH and $\Delta S > 0$).

A prominent example of a low ceiling temperature vinyl monomer is α-methyl-
styrene (0°C at 0.8 M). There is, however, a long row of cyclic monomers which
are characterized by low ceiling temperature, i.e., tetrahydrofuran, lc, 80°C; dioxo-

lan, ls, 165°C; cyclopentene, lc, 97°C (l, liquid monomer; c/s, crystalline/solid polymer) [1].

Thus, particularly for cyclic monomers, the ring-closing depolymerization reaction should offer a concept for recycling of suitable polymers.

RING-OPENING POLYMERIZATION REACTIONS

Ring-opening polymerization reactions can be achieved by radical, cationic, anionic, and metal-organic initiators. Equation (4) shows two examples of radical polymerization as developed by Bailey [2].

$$(4a)$$

$$(4b)$$
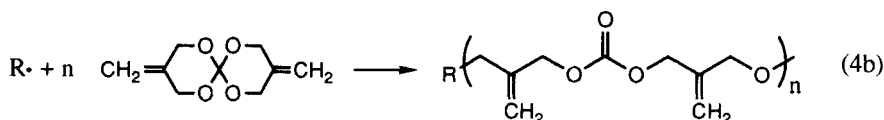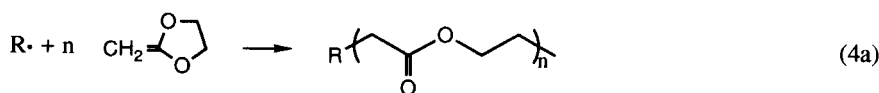
Equation (5) indicates the cationic ring-opening polymerization of dioxolane [3].

$$(5)$$
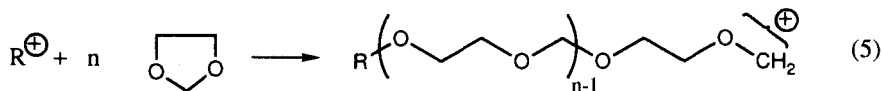
Equation (6) shows the ring-opening polymerization of a cyclic carbonate [4].

$$(6)$$
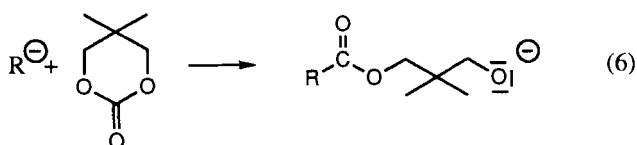
Last but not least, the metathesis polymerization of cycloolefins is a ring-opening polymerization as indicated by Eq. (7) [5].

$$(7)$$
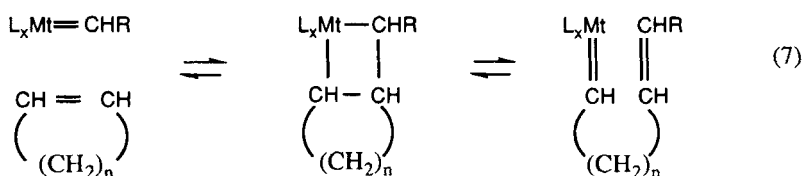
It should be mentioned that in a kinetically controlled regime, all these reactions may yield only high polymers, even living polymers, as indicated by Eq. (8) [6].

(8)

RING-CHAIN EQUILIBRIUM

Monomer–polymer equilibrium is not the only equilibrium observed in ring-opening polymerization. There is a second equilibrium to be considered, i.e., ring–chain equilibrium. As indicated by Eq. (9), the equilibrium constant of a certain cyclic R_x with degree of polymerization x is to a first approximation equal to the equilibrium concentration of the respective cycle.

$$P_n \rightleftharpoons P_{n-x} + R_x \tag{9}$$

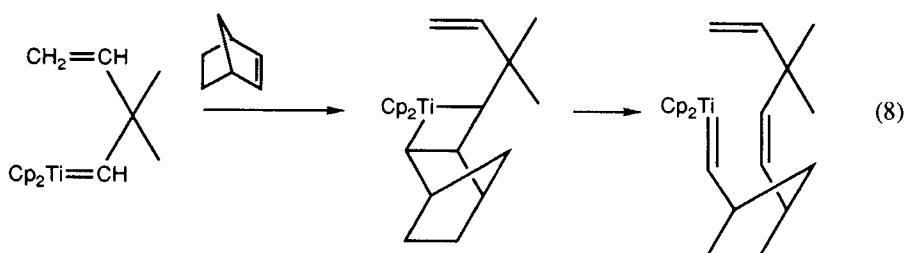According to Jacobson and Stockmayer [7] the equilibrium constant is determined by Eq. (10) and is proportional to the degree of polymerization to the -2.5 power.

$$K_x = [P_{n-x}][R_x]/[P_n] \approx [R_x] = [3/(2N)]^{2/3} \cdot 1/(2Nx) \cdot (1/<r_x^2>)^{3/2} \tag{10}$$

$$K_x \approx 1/x^{5/2}$$

with $[R_x]$ being the equilibrium concentration of the cyclic oligomer with degree of polymerization x, N the number of bonds of the oligomer, and $<r_x^2>$ the mean square radius of gyration of a polymer segment with degree of polymerization x.

It has been shown that for the metathesis reaction of cyclic olefins, ring–chain equilibrium can be achieved by starting from the monomer, any oligomer, and the polymer as well. The Jacobson–Stockmayer equation is very well fulfilled for higher oligomers. However, equilibrium is not achieved instantaneously in any case. In particular, for the ring-opening polymerization of norbornene, high polymers are obtained in the first place and a degradation of the polymer in the presence of active catalyst only occurs upon prolonged reaction times [8].

Thus, the polymerization of cycloolefins may proceed when the rate constant of insertion of a monomer is much larger than the rate constant of back-biting, resulting in high molecular weight material and a polymerization mode corresponding to a chain-growth reaction. On the other hand, the rate constant of the back-biting reaction may be much larger than that of the insertion reaction, and this results in a kinetically enhanced homologous series of cyclic oligomers which are then progressively converted into a high polymer approaching ring–chain equilibrium. This reaction mode rather resembles stepwise polymerization [9].

Another example is the anionic ring-opening polymerization of cyclic carbonates as indicated by Eq. (6). Ring–chain equilibrium is established by intra- and intermolecular reactions.

The homologous series of cyclic oligomers was analyzed by means of gel permeation chromatography. The Jacobson–Stockmayer plot shows a perfect

straight line with a slope of -2.5 with the exception of the low molecular weight oligomers (dimer, trimer) for which the conditions of the theory, i.e., Gaussian chain statistics, are not fulfilled [10].

The ring-opening polymerization of cyclic carbonates is characterized by an alcoholate anion as the active species. Thus, it can be initiated by such suitable prepolymers as polyethylene oxide and polytetrahydrofuran with one or two alcoholate chain ends to achieve block copolymers. A suitable telechelic polydimethylsiloxane can be used as the initiator as well. The rate constant of polymerization of a cyclic carbonate is significantly influenced by the type of prepolymer (initiator). In the case of polyethylene oxide, the counterion is solubilized by the prepolymer chain which increases the nucleophilicity of the alcoholate chain end (1); in the case of the siloxane prepolymer, the alcoholate anion is complexed by the silicon atom, thus decreasing the nucleophilicity of the chain end (2). The polytetrahydrofuran chain exerts no influence on the rate of polymerization of cyclic carbonate [11].
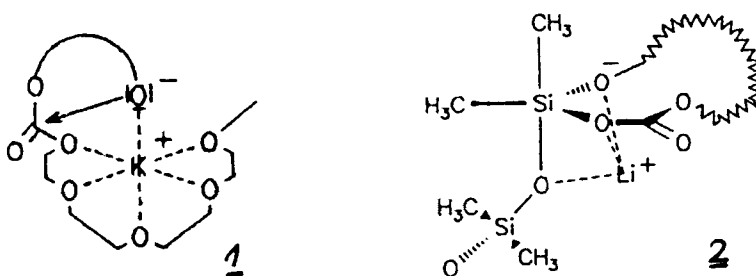
The anionic ring-opening polymerization of cyclic carbonates can be combined with the ring-opening polymerization of such lactones as pivalolactone and ϵ-caprolactone to yield block or statistical copolymers [12,13].

DEPOLYMERIZATION

The undesired depolymerization of polyoxymethylene is known as is the depolymerization of positive resist copolymers such as the alternating copolymer of butene-1 and SO_2. Further, acrylic acid is produced via depolymerization of the polymer which forms spontaneously from propiolactone obtained by reaction of ketene and formaldehyde. The depolymerization is complete at 150°C.

Cyclic carbonates are usually prepared by depolymerization of the polymer which is obtained by a polycondensation reaction. Consequently, the aliphatic polycarbonates obtained by anionic ring-opening polymerization can be depolymerized at temperatures above 250°C in the presence of catalysts such as $Bu_2Sn(OCH_3)_2$, which is known to be an efficient transesterification catalyst.

By using such strong acids as CF_3SO_3H or the respective anhydride, polytetrahydrofuran can be depolymerized at temperatures above 150°C.

Potassium hydroxide is an efficient catalyst for the depolymerization of polydimethylsiloxane at temperatures above 200°C. In contrast to the two former examples, however, a homologous series of cyclic oligomers is obtained.

Beside the homopolymers, block copolymers are also eligible for depolymeri-

zation reactions. Thus, the ABA triblock copolymer of tetrahydrofuran with carbonate blocks at both ends is depolymerized in the presence of $CF_3SO_3CH_3$ at 150°C within 30 minutes; tetrahydrofuran is obtained in the first fraction, and dimethyltrimethylene carbonate is found in the second fraction after the addition of $Bu_2Sn(OCH_3)_2$ and increasing the temperature to 250°C.

The triblock copolymer of polydimethylsiloxane with a carbonate block at each end is depolymerized within 1 hour in the presence of potassium hydroxide at 260°C. The first fraction contains 83% cyclic siloxanes, and the second fraction, obtained at 280°C, contains 52% cyclic carbonate. The reduced depolymerization rate of the polycarbonate is due to complexing of the alcoholate anions by silicon.

OUTLOOK

So-called energetic recycling is certainly an important pathway for getting rid of used polymers, in particular, after incineration processes which are not harmful to the environment have been developed. To a similar degree, pyrolytic processes warrant attention. The reprocessing recycling is often connected with down-cycling of a material. In contrast, the thermodynamic recycling concept has to be considered as an intelligent method although it is only applicable in particular cases. None of these different concepts will be able to solve the waste problem individually, but a combination of concepts might be able to solve the highly differentiated problems of our future.

ACKNOWLEDGMENTS

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