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# Polymerization Initiated with a Potassium Complex of Aromatic Ketone and Its Use in the Preparation of a Multi-Chain Copolymer

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Four kinds of complexes were prepared by the reactions of benzil with a potassium or potassium-sodium alloy in tetrahydrofuran. The polymerizations of styrene (St), isoprene (Ip), methyl methacrylate (MMA), and ε-caprolactone (CL) initiated with these complexes were attempted. St and Ip were found to be polymerized by the dipotassium or tetrapotassium adducts of benzil, but not by the monopotassium ketyl. All these complexes were effective in polymerizing MMA and CL. A new class of multi-chain copolymers with different kinds of branches was also prepared by the polymerizations of MMA and CL with the potassium adducts of polystyrene ketones synthesized by the coupling reactions of one-ended living polystyrene with 2, 4′-dichlorobenzophenone or terephthaloyl chloride.

Some studies of the syntheses of star-type branched polymers by means of anionic living polymerizations and of their characterizations have been recently developed.1-5) Polymerizations or graft copolymerizations initiated by the alkali metal complexes of aromatic ketone or of polyvinyl benzophenone have also been studied.6-13)

The present paper is concerned with the relation between the structures of the active species of some potassium complexes of aromatic ketones and their polymerizing ability with regard to several monomers, and with an attempt to obtain a new class of multi-chain copolymers with different kinds of branches, starting from the potassium adducts of polystyrene ketone possessing one or two carbonyl groups in the middle part of the chain.

## Experimental

**Materials.** Styrene (St), isoprene (IP), methyl methacrylate (MMA), and ε-caprolactone (CL) were purified by the usual methods. Tetrahydrofuran (THF) was distilled after refluxing it with sodium. The monomer and the solvent were directly introduced into a polymerization vessel by distillation from calcium hydride (in the case of the monomer) or from sodium-naphthalene (the solvent) after evacuation by repeated freezing and thawing in a vacuum line ($10^{-6}$ mmHg).

Benzil, terephthaloyl chloride, and 2, 4′-dichlorobenzophenone were recrystallized from ethanol, *n*-hexane, and petroleum ether respectively. The methyl phenyl isopropenyl ether was synthesized according to the method of Ziegler *et al.*14)

**Polymerization Procedures.** The general experimental techniques for a homogeneous anionic polymerization developed by Szwarc15) and by Morton *et al.*16) were employed in the present investigation.

Potassium complexes of benzil were prepared by the reaction of benzil with a potassium or potassium-sodium alloy in THF *in vacuo*. The solution of potassium complexes of benzil in THF was divided into several ampoules through a sintered glass filter under a vacuum; it could then be used in the following reactions.

Phenyl isopropyl potassium was prepared by the reaction of methyl phenyl isopropenyl ether with potassium in THF *in vacuo*. This solution was also filtered through a sintered glass filter in order to remove the small amount of potassium methoxide formed in the reaction.

The polymerizations of St, Ip, MMA, and CL initiated by the potassium complexes of benzil were performed by the same procedures as those used for

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the polymerizations of lactones by living polymer anions described in a previous paper.17)

One-ended living polystyrene, prepared from the reaction of St with phenyl isopropyl potassium in THF, was coupled with 2,4′-dichlorobenzophenone or terephthaloyl chloride, resulting in the formation of polystyrene ketones with one or two carbonyl groups in the middle part of the chains. In each of the processes, the solution of the coupling agent was added slowly to the solution of living polystyrene until its red color disappeared.

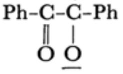
Potassium adducts of polystyrene ketones were obtained by the reactions of polystyrene ketones with potassium in THF. The polymerizations of CL, MMA, and St initiated by these adducts were performed in a vacuum system at room temperature. Each of the resulting gross polymers was separated into three or four fractions using an extraction technique.

**Solution Viscosity.** The viscosities of polystyrene in cyclohexane were measured at 34.5°C using an Ubbelohde-type viscometer in three to four concentrations, $c$, below about 1 g/100 m$l$. The intrinsic viscosities, $[\eta]$, were determined by the extrapolation of the curves of $\eta_{sp}/c$ *vs.* $c$ to $c=0$. The molecular weights of polystyrene were calculated from the following equation18) using the viscosity data.

$$[\eta]_\theta = 8.5\times10^{-4}M^{0.5} \quad \text{(cyclohexane, 34.5°C)}$$

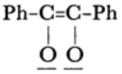
## Results and Discussion

**Preparation of Potassium Complexes of Benzil.** The results of the reactions of benzil with a potassium or potassium-sodium alloy in THF are shown in Table 1. Four kinds of benzil potassium complexes were formed, according to the conditions.



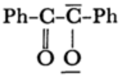
$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{\underline{O}}{|}}{\dot{C}}{-}Ph}$

I



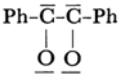
$\mathrm{Ph{-}\underset{\underset{\underline{O}}{|}}{C}{=}\underset{\underset{\underline{O}}{|}}{C}{-}Ph}$

II



$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{\underline{O}}{|}}{\overline{C}}{-}Ph}$

III



$\mathrm{Ph{-}\underset{\underset{\underline{O}}{|}}{\overline{C}}{-}\underset{\underset{\underline{O}}{|}}{\overline{C}}{-}Ph}$

IV

Figures 1, 2, and 3 show the ultraviolet and visible absorption spectra of these benzil potassium complexes. The molar ratios of benzil to potassium in the complexes were determined by alkalimetry. From the facts that (i) the benzil potassium complex I was able to initiate the polymerizations of MMA and CL, but not the polymerizations of St and Ip (Table 2); (ii) the dipotassium complex of benzil obtained here induced the polymerizations of MMA, CL, St, and Ip, as will be shown in the following section and (iii) the structure II was also given for the benzil dianion,19)

TABLE 1. PREPARATION OF BENZIL POTASSIUM COMPLEXES

| No. | Benzil-THF soln., mol/$l$ | K | Temp. °C | Time hr | Benzil/K molar ratio c) | ESR signal d) | Structures of benzil potassium complexes |
|---|---|---|---|---|---|---|---|
| 1 | 0.0169 | Equivalent | −78 | 15 | 4.2/1 | ○ | I |
| 2 | 0.0084 | Excess | −78 | 4 | 1/1.0 | ○ | I |
| 3 | 0.0179 | Excess | r.t. b) | 50 | 1/1.7 | ○ | I+II+III |
| 4 | 0.0178 | Excess a) | r.t. b) | 150 | 1/4.8 | ○ | IV |

a) Potassium-sodium alloy.
b) Room temperature.
c) Determined by alkalimetry.
d) Qualitative representation.

TABLE 2. POLYMERIZATIONS WITH BENZIL POTASSIUM KETYL AT ROOM TEMPERATURE

| Initiator soln., m$l$ | Monomer, | g | THF m$l$ | Time hr | Yield g | Convn. % |
|---|---|---|---|---|---|---|
| 10 a) | St | 2.72 | 10 | 3 | 0 | 0 |
| 5 b) | St | 3.17 | 10 | 6 | 0 | 0 |
| 10 a) | Ip | 2.72 | — | 6 | 0 | 0 |
| 5 b) | Ip | 2.72 | 10 | 4 | 0 | 0 |
| 5 a) | MMA | 2.90 | 10 | 3 | 0.88 | 30.4 |
| 5 b) | MMA | 2.81 | 10 | 2 | 2.29 | 81.6 |
| 10 a) | CL | 3.23 | 25 | 1 | 2.77 | 85.7 |
| 5 b) | CL | 3.13 | 50 | 0.5 | 3.08 | 98.6 |
| 5 b) | MMA-St c) | 2.81—2.76 | 25 | 0.25 | 2.64 | 47.4 |

a) Benzil : potassium, 4.2: 1 (mol).
b) Benzil : potassium, 1: 1 (mol).
c) Copolymerization of MMA with St.

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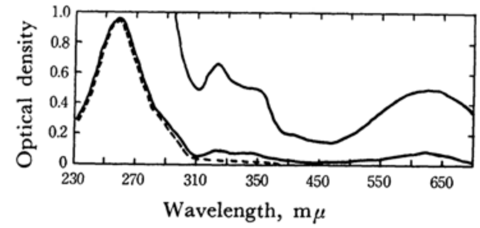


Fig. 1. Ultraviolet and visible absorption spectra of benzil potassium ketyl and benzil.

—— Benzil potassium (4.2:1) ketyl
---- Benzil

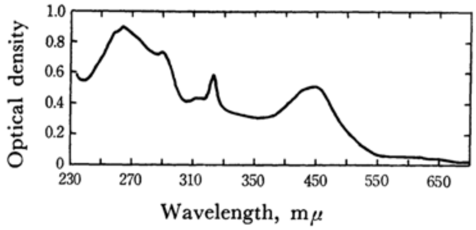


Fig. 2. Ultraviolet and visible absorption spectrum of benzil potassium (1:1) ketyl.

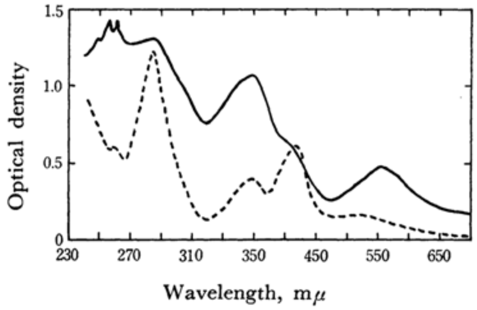


Fig. 3. Ultraviolet and visible absorption spectra of benzil potassium adducts.

it may be thought that the initiator III, having a carbanion structure, can initiate the polymerizations of St and Ip, while the initiators I, II, and III, having alcoholate anions, are active for MMA and CL, listed in Run No. 3 in Table 1. The benzil potassium complex with more than four mole of potassium per mole of benzil revealed an ESR signal. This may suggest some possibility of the existence of some higher potassium adducts of benzil other than the complex IV in the complex. The further investigation of this possibility must be the subject of future research.

**Polymerizations with Potassium Ketyl of Benzil.** Table 2 lists the results of the polymerizations of St, Ip, MMA, and CL and of the copolymerization of MMA with St initiated by the benzil potassium ketyl prepared in Experiments No. 1 and 2 in Table 1.

It may be seen from Table 2 that the polymerizations of MMA and CL can be easily initiated by these ketyls, but not those of St and Ip. The product of the St-MMA copolymerization was found, from the infrared analysis, to be virtually only the MMA homopolymer. These facts suggest that alcoholate anions of the ketyl radical anions predominantly participate in the initiations.

**Polymerizations with a Dipotassium Adduct of Benzil.** The results of the polymerizations of St, Ip, MMA, and CL using a benzil dipotassium adduct (No. 3 in Table 1) at room temperature are listed in Table 3.

TABLE 3. POLYMERIZATIONS WITH BENZIL DIPOTASSIUM ADDUCT AT ROOM TEMPERATURE

| Initiator soln., *ml* | Monomer | g | THF *ml* | Time hr | Yield g | Convn. % |
|---|---|---|---|---|---|---|
| 5.25 | St | 2.72 | 25 | 2 | 2.66[a] | 98.0 |
| 5.15 | Ip | 2.69 | 25 | 2 | 2.51 | 93.3 |
| 5.00 | MMA | 1.58 | 25 | 1 | 1.51 | 95.6 |
| 5.00 | CL | 3.07 | 25 | 1 | 2.57 | 83.7 |

a) Molecular weight of polystyrene obtained by viscometry, 490000.

It may be noted in Table 3 that St and Ip, as well as other monomers, could be easily polymerized by a dipotassium adduct of benzil. This phenomenon is similar to that induced by the dialkali metal adduct of benzophenone. Some amounts of benzil potassium ketyl may also be assumed, from the results of alkalimetry and from the ESR measurements, to be included in the initiator. A living polymer is also considered to be formed in the polymerization of St with the dipotassium adduct of benzil, since it occurs in the case of the dialkali metal adduct of benzophenone. The amount of the active species taking part in the initiation of the polymerization was estimated, from a comparison of the molecular weight of polystyrene (490000) (viscometry) with that obtained by assuming that all active species have the structure III (44000), to be lower than 10% of the initiator.

**Polymerizations with Tetrapotassium Adduct of Benzil.** The tetrapotassium adduct of benzil initiates the polymerization of St as well as of MMA and CL at room temperature, as is shown in Table 4.

TABLE 4. POLYMERIZATIONS WITH BENZIL TETRAPOTASSIUM ADDUCT AT ROOM TEMPERATURE

| Initiator soln., *ml* | Monomer | g | THF *ml* | Time hr | Yield g | Convn. % |
|---|---|---|---|---|---|---|
| 8.05 | St | 2.76 | 23.7 | 1 | 2.70[a] | 97.8 |
| 4.80 | MMA | 1.52 | 28.7 | 1 | 1.34 | 88.2 |
| 4.88 | CL | 3.13 | 27.5 | 1 | 3.04 | 97.1 |

a) Molecular weight of polystyrene obtained by viscometry, 89000

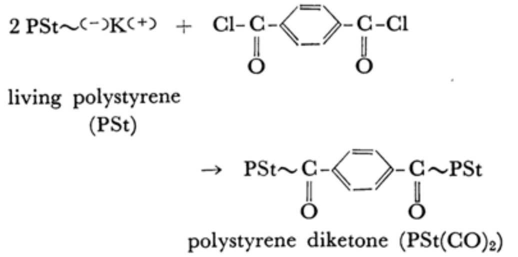
It may be concluded from the results described above that the polymerizations of St and Ip are initiated only by the carbanion, although those of MMA and CL can be easily initiated by both the alcoholate anion and the carbanion of potassium complexes of benzil. The polystyrene and polymethyl methacrylate obtained with a tetrapotassium adduct of benzil was light red even after reprecipitation in a benzene-methanol system. The initiator seems, therefore, to be incorporated in the polymer. The facts that the coloration due to the initiator also remained in the polymerization system and that there was a considerable difference between the molecular weights (89000) of the polystyrene obtained from viscosity measurements and those (19000) obtained by calculating from the amount of the initiator used, suggest that not all of the potassium complexes of benzil can always participate in the initiation because of some resonance stabilization which may exist in these complexes, and also that the rate of propagation is higher than that of initiation.

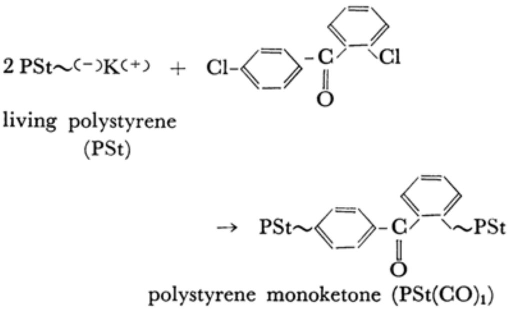
**Preparation of Polystyrene Ketone.** A one-ended living polystyrene was prepared by the polymerization of St by the use of phenyl isopropyl potassium in THF. The results are shown in Tables 5 and 6.

TABLE 5. PREPARATIONS OF PHENYL ISOPROPYL POTASSIUM

| No. | Methyl phenyl isopropenyl ether ml | THF ml | K g | Temp. °C | Time hr |
|---|---|---|---|---|---|
| 1 | 2.00 | 57.0 | 1.35 | −78 | 46 |
| 2 | 2.06 | 102.7 | 1.54 | −78 | 30 |

Polystyrene ketones with one or two carbonyl groups in the middle part of the chains were obtained by the coupling reactions of the living polystyrene with 2, 4′-dichlorobenzophenone or terephthaloyl chloride at room temperature.





The results of the coupling reactions are shown in Tables 7 and 8.

When the molecular weight of the reaction product was smaller than twice that of the parent living polystyrene, it was fractionated in a benzene-methanol system to remove any lower-molecular-weight polystyrene. The molecular weights of the polystyrene ketone thus obtained were almost twice those of the parent living polystyrene. Although no characteristic absorption of the carbonyl group appeared in the IR spectra of the resulting polystyrene ketone, a broad absorption band of polystyrene ketone could be observed in the 300—400 mμ region, in which polystyrene did not show any absorption at all, in the ultraviolet and the visible absorption spectra.

**Preparation of Polystyrene Ketone Potassium Adducts.** Tables 9 and 10 represent the results of the reactions of polystyrene ketones with potassium in THF.

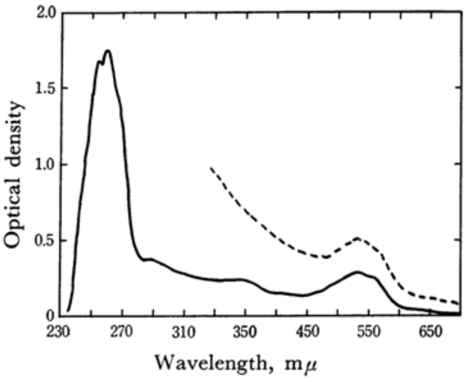


Fig. 4. Ultraviolet and visible absorption spectra of polystyrene ketone potassium adducts.
—— Polystyrene diketone potassium adduct
---- Polystyrene monoketone potassium adduct

TABLE 6. PREPARATIONS OF ONE-ENDED LIVING POLYSTYRENE

| Phenyl isopropyl Potassium-THF soln. ml | No. of Table 5 | St g | THF ml | Temp. °C | Time hr | MW of polystyrene |
|---|---|---|---|---|---|---|
| 28.6 | 1 | 5.85 | 180.0 | −78 | 3 | 31600 |
| 25.0 | 2 | 8.34 | 183.3 | −78 | 3 | 13800 |

TABLE 7. COUPLING REACTIONS OF LIVING POLYSTYRENE WITH TEREPHTHALOYL CHLORIDE (TPC)[a]

| Living PSt-THF soln., ml | PSt g (MW) | TPC-THF soln. ml | TPC ml | Yield g | MW of PSt ketone |
|---|---|---|---|---|---|
| 50.5 | 1.78(31600) | 36.9 | 5.3 | 1.69[b] | 56600[b] |
| 101.1 | 3.90(13800) | 62.6 | 78.2 | 1.73[c] | 26200[c] |

a) At room temperature; 3 hr.
b) For the unfractionated product.
c) After fractionation in benzene-methanol system.

TABLE 8. COUPLING REACTION OF LIVING POLYSTYRENE WITH 2, 4′-DICHLOROBENZOPHENONE (DCBP)[a]

| Living PSt-THF soln., ml | PSt g (MW) | DCBP-THF soln. ml | DCBP mg | Yield g | MW of PSt ketone |
|---|---|---|---|---|---|
| 49.0 | 1.72(31600) | 9.7 | 2.0 | 0.92[b] | 64600[b] |

a) At room temperature; 3 hr.
b) After fractionation in benzene-methanol system.

The various colored solutions were formed under different experimental conditions, as Table 9 shows. It was observed that the initial dark yellow color gradually changed to a light red one. The reddish-colored solution did not reveal an ESR signal. The solution of the polystyrene monoketone potassium adduct showed the same light-red color. Figure 4 illustrates the ultraviolet and the visible absorption spectra of polystyrene ketone potassium adducts. The maximum absorption appears at 536 m$\mu$ in every reddish solution of the potassium adducts of the mono- and the di-ketone. This absorption may be thought to be due to the carbanion of the adduct which has two potassium atoms per carbonyl group of polystyrene ketone.[20–22]

**Syntheses of Branched Copolymers.** Table 11 shows the results of the polymerizations of St, MMA, and CL with polystyrene diketone potassium adducts at room temperature.

The molecular weight of the multi-chain polystyrene obtained by viscometry was 693000; this is in good agreement with the value of 844000 calculated from the carbanion concentration of the polystyrene diketone potassium adduct.

The gross polymer obtained in the PSt-CL system was elution-fractionated, using methanol, cyclohexane, and acetic acid as solvents, into the four parts to be described below; each fraction was identified by infrared analysis. After removing 0.49 g of the CL oligomer as a methanol-soluble fraction, 0.26 g of polystyrene as a cyclohexane-soluble fraction, and 1.53 g of the CL homopolymer as a cyclohexane insoluble- and an acetic acid-soluble fraction, these remained 0.29 g of the PSt-PCL branched copolymer as a fraction insoluble in both solvents. The molecular weight

TABLE 9. PREPARATIONS OF POLYSTYRENE DIKETONE POTASSIUM ADDUCT

| No. | PSt(CO)$_2$ g | (MW) | PSt(CO)$_2$-THF soln., ml | K g | Temp. °C | Time hr | Color |
|---|---|---|---|---|---|---|---|
| 1 | 1.139 | (56600) | 110.0 | 0.38 | 0 | 6 | dark yellow |
| 2 | 0.094 | (56600) | 9.0 | 0.44 | r.t.[a] | 60 | light red |
| 3 | 0.103 | (56600) | 24.5 | 0.60 | r.t.[a] | 48 | light red |

a) Room temperature.

TABLE 10. PREPARATIONS OF POLYSTYRENE MONOKETONE POTASSIUM ADDUCT

| No. | PSt(CO)$_1$ g | (MW) | PSt(CO)$_1$-THF soln., ml | K g | Temp. °C | Time hr | Color |
|---|---|---|---|---|---|---|---|
| 1 | 0.720 | (64600) | 112.9 | 0.29 | 0 | 20 | light red |
| 2 | 0.060 | (64600) | 9.0 | 0.55 | 0 | 20 | light red |

TABLE 11. POLYMERIZATIONS WITH POLYSTYRENE DIKETONE POTASSIUM ADDUCT AT ROOM TEMPERATURE

| PSt(CO)$_2$-K adduct-THF soln., ml | Preparation No. of Table IX | PSt(CO)$_2$ g | Monomer | g | THF ml | Time hr | Yield g | Convn. % |
|---|---|---|---|---|---|---|---|---|
| 24.5 | 3 | 0.103 | St | 1.67 | — | 1 | 1.65 | 91.7 |
| 56.0 | 1 | 0.580 | MMA | 2.71 | 50.0 | 5 | 1.77 | 43.8 |
| 53.2 | 1 | 0.551 | CL | 3.23 | 47.7 | 5 | 2.66 | 65.3 |

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TABLE 12. POLYMERIZATIONS WITH POLYSTYRENE MONOKETONE POTASSIUM ADDUCT AT ROOM TEMPERATURE

| $PSt(CO)_1$-K adduct-THF soln., ml | $PSt(CO)_1$ g | Monomer | g | THF ml | Time hr | Yield g | Convn. % |
|---|---|---|---|---|---|---|---|
| 56.4 | 0.360 | CL | 3.18 | 49.1 | 5 | 1.04 | 21.3 |
| 54.2 | 0.346 | MMA | 1.76 | — | 5 | 0.58 | 13.2 |

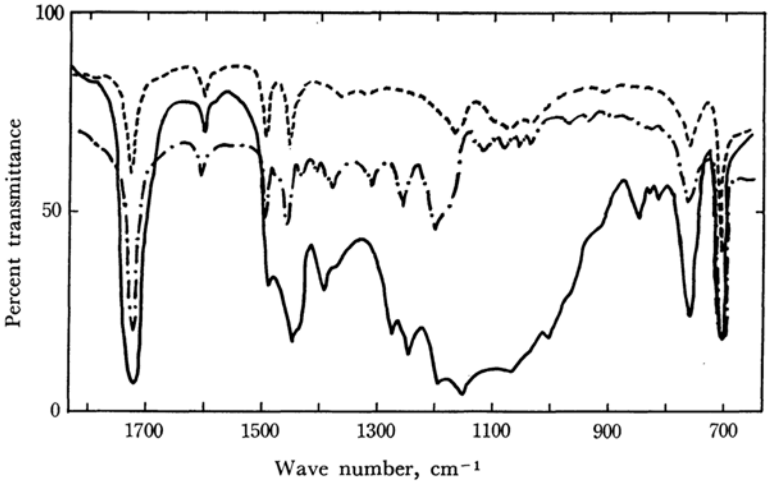

Fig. 5. Infrared absorption spectra of branched copolymers.

·—· Polystyrene diketone-PCL branched copolymer
—— Polystyrene diketone-PMMA branched copolymer
---- Polystyrene monoketone-PCL branched copolymer

of the PSt-PCL branched copolymer, as calculated from the results of an elementary analysis, was 80700 (63200 for the PSt part and 17500 for the PCL part).

The gross polymer obtained in the PSt-MMA system was also elution-fractionated. After 0.95 g of PMMA as an acetonitrile-soluble fraction and 0.51 g of PSt as an acetonitrile-insoluble and cyclohexane-soluble fraction had been removed, 0.14 g of the PSt-PMMA branched copolymer was obtained as a fraction insoluble in both solvents. The molecular weight of the branched copolymer, as obtained by an elementary analysis, was 338800 (63200 for the PSt part and 275600 for the PMMA part).

Table 12 shows the results of the polymerizations of MMA and CL using polystyrene monoketone potassium adducts at room temperature.

The gross polymers obtained here were also elution-fractionated using the same solvents as have been described above. In the PSt-CL system we obtained 0.37 g of the CL oligomer, 0.31 g of PSt, 0.22 g of PCL, and 0.02 g of the PSt-PCL branched copolymer. The molecular weight of the PSt-PCL branched copolymer was calculated, from the results of an elementary analysis, to be 120500 (63200 for the PSt part and 57300 for the PCL part). In the PSt-MMA system we obtained 0.21 g of PMMA, 0.31 g of PSt, and 0.01 g of the PSt-PMMA branched copolymer. The infrared absorption spectra of the branched copolymers are shown in Fig. 5. Each spectrum shows the absorption bands, characteristic of carbonyl groups at 1730 $cm^{-1}$, of ester groups at 1150 and 1250 $cm^{-1}$, and of PSt units at 700, 755, 1030, 1495, and 1603 $cm^{-1}$.